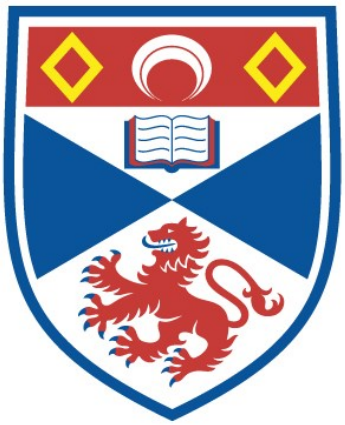
AZULENES WITH SPECIAL REFERENCE TO THE ACTION OF ELECTROPHILIC REAGENTS

Edward Cameron Kirby

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1961

AZULENES - WITH SPECIAL REFERENCE TO THE ACTION OF ELECTROPHILIC REAGENTS

being a Thesis presented by

EDWARD CAMERON KIRBY

to the University of St. Andrews in application for the degree of Ph.D.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

C E R T I F I C A T E.

I certify that Edward C. Kirby has spent nine terms at research work under my direction, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews) and is qualified to submit the accompanying Thesis in application for the degree of Ph.D.

[redacted]

Director of Research.

4th September 1961.

D E C L A R A T I O N.

I hereby declare that the following Thesis is a record of the results of experiments carried out by me, and further that the Thesis is my own composition and has not previously been presented for a higher degree.

The research was carried out in the Department of Chemistry, United College, University of St. Andrews under the direction of Dr. D. H. Reid.

4th September. 1961.

UNIVERSITY CAREER.

I first matriculated in the United College of St. Salvator and St. Leonard, University of St. Andrews, in October 1954, and subsequently graduated B.Sc. with Second Class Honours in Chemistry in July 1958.

I was admitted as a Research Student in the Department of Chemistry, United College, St. Andrews, in October 1958.

I was awarded a Research Studentship by the Department of Scientific and Industrial Research for whole of my period as a Research Student.

ACKNOWLEDGEMENTS.

My deep gratitude is extended to Dr. D. H. Reid of the Chemistry Department, University of St. Andrews, for assistance and guidance given to me during the prosecution of the work embodied in this Thesis, and for his never failing enthusiasm, which illuminated the intense beauty of organic chemistry.

I am grateful to the Department of Scientific and Industrial Research for the award of a Research Studentship during the period of my research programme.

I should like to thank the members of the Technical Staff of the Chemistry Department of St. Andrews University who gave of their services, in particular, Mr. M. Zowchowski for recording the bulk of the infra-red spectra, and Messrs. R. Morris and J. Bayne for carrying out the photography required for the presentation of this Thesis. Help with the operation of the Pye Argon Chromatograph from Dr. P.J. Sykes is gratefully acknowledged. I am indebted to Mrs M. Liggett who undertook most of the typing of the manuscript.

I thank Professor John Read, F.R.S., for his permission to carry out these researches in the Chemistry Department, St. Andrews.

University of St. Andrews.
August, 1961.

PUBLICATIONS.

E. C. Kirby and D. H. Reid, Conjugated Cyclic Hydrocarbons and their Heterocyclic Analogues, Part II. The Condensation of Azulenes with Homocyclic and Heterocyclic Aromatic Aldehydes in the Presence of Perchloric Acid. J., 1960, 494.

Part IV. Dimethine Cyanine Salts from the Condensation of 1-Formylazulenes with Heterocyclic Quarternary Ammonium Salts. J., 1961, 163.

Part V. 1,1'-Azulenylmethyleneazulenium Salts and 1-Ethoxymethyleneazulenium Salts. J., 1961, 1724.

Part VI. The Condensation of Azulenes with Aliphatic Aldehydes in the Presence of Perchloric Acid. J., 1961,

E. C. Kirby and D. H. Reid, 4,6,8-Trimethylazulenium Perchlorate. Chem. Ind., 1960, 1217.

E. C. Kirby and D. H. Reid, Hydride Hyperconjugation in 1(3)-Methylazulenes. Tetrahedron Letters, 1960, 27, 1.

EXPLANATORY NOTE.

This Thesis comprises four Parts, A,B,C, and D. Each Part is divided into sections prefixed by Roman numerals, and some of these sections have been further divided into sub-sections, prefixed by Arabic numerals. Reference to another place in the Thesis is thus made (in parentheses) by a unique combination of a capital letter, a Roman numeral, and, if necessary, an Arabic numeral, e.g., (AVII4) - Nitration of Azulenes.

Structural formulae, figures, and tables are numbered independently (with Arabic numerals) within each Part. Subdivision of formulae numbers with letters (e.g., 64a and 64b, Part B) is used to distinguish alternative canonical structures. References to the chemical literature are consecutive throughout the Thesis, and each reference is indicated by a number in superscript, a key to which is given at the end of the Thesis under "Literature Cited".

Part A commences with a brief historical survey of the chemical literature of the azulenes, and their occurrence, both natural and otherwise. A consideration of theoretical concepts of the structure of azulene, and its relationship to other carbocyclic systems, follows, with a brief review of the properties of azulenes.

Part B is a discussion of the results achieved in the

course of investigations centred on the reaction of azulenes with electrophilic reagents.

Part C is devoted to a description of experimental details, and is the complement to Part B, while Part D describes the preparation of starting materials and intermediates.

A number of Plates, mainly of visible absorption spectra, are to be found at the end of the thesis.

CONTENTS.

PART A.

P A R T A.

AI Azulenes; Historical Introduction

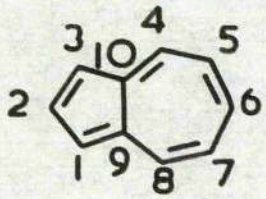
For several hundred years it had been noticed that certain essential oils contain deep blue substances, or give rise to such when treated with acids and oxidising agents. In 1863[1] the generic name "azulene" was applied to the compounds responsible for the blue colour, and it was later estimated[2] that 20% of the essential oils described contained azulenes or azulene precursors.

The chemical study of these compounds began with Sherndal's observation[3] that they are reversibly soluble in strong acids. This provided a means of separating them from the essential oils. Sherndal also made use of their typically aromatic property of forming complexes with picric acid and sym-trinitrobenzene. This was used both to assist their purification, and to determine their molecular weights. It was further proposed[3] that the azulenes are structurally related to the sesquiterpenes which generate them, and that a novel structure must be present, since the intensity of colour was exceptional for the size of molecule.

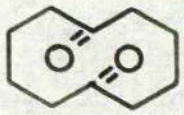
Following this work, Ruzicka and Rudolph[4] concluded from degradative experiments on azulene and partially hydrogenated azulenes, that they contained a hitherto unknown bicyclic system with no benzene ring.

Finally, St. Pfau and Plattner[2] proposed that the parent hydrocarbon, azulene, is the fully conjugated bicyclic

structure (1), derived by fusion of a five and a seven-membered ring. This was confirmed

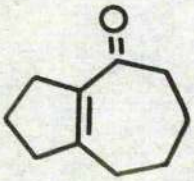


(1)

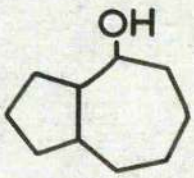


(2)

by a synthesis of azulene and several 4-substituted azulenes from 9,10-octalin[2,5]. Ozonolysis of this hydrocarbon gave the diketone (2)[6] which was cyclised[7] by aqueous sodium carbonate to (3). This ketone was reduced with sodium and ethanol to the alcohol (4) which, on dehydration and dehydrogenation with palladium-charcoal, yielded azulene (1)[5].



(3)



(4)

The 4-phenyl, 4-methyl, and 4-ethyl-derivatives were prepared[2] by treating the ketone (3) with the appropriate Grignard reagents before dehydration and dehydrogenation.

Following this pioneering work, many papers were published in this field during the succeeding thirteen years, mainly concerned with synthetic routes to azulene and its derivatives. These are briefly reviewed in (AIV1). The most important

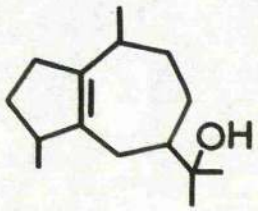
observations concerning the properties of azulenes which emerged from the studies of this period (1936-1949) were expressed in the generalisations known as the Plattner rules[8] which rationalised the spectral data of alkylated azulenes (see AV).

During the past decade more attention has been turned towards the fundamental properties and chemical behaviour of azulenes, and this started with a more sophisticated examination of the phenomenon of reversible solubility in acids[9].

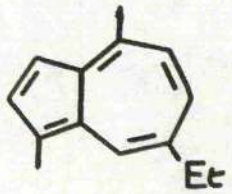
The modern concepts of the fine structure of azulene, derived from the results of investigations of recent years is discussed in the following sections.

AII Azulenes: Natural Occurrence

The azulene nucleus, and more particularly its sesquiterpene precursors, occur quite widely in nature. The essential oil from the wood of Guaiacum Officional L. is one example of many which yield azulene precursors. Guaiol (5) is a major constituent of it. Chamazulene

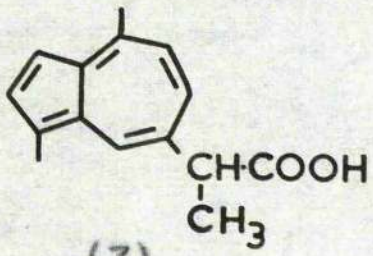


(5)

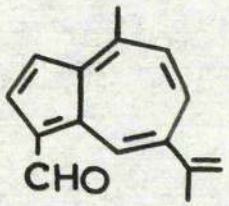


(6)

(6) can be obtained directly, in low yield, by the distillation of camomile oil, obtained from Matricaria Camomilla L., and under milder conditions the acid (7) may be isolated[10].

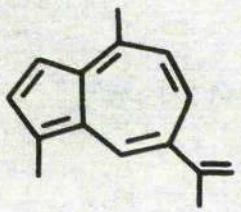


(7)

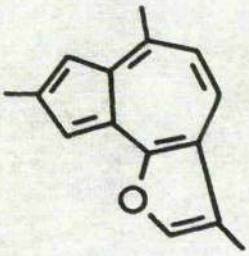


(8)

The edible orange fungus Lactarius deliciosus L. yields, among other things, a mixture of lactaroviolin (8) and lactarazulene (9)[11]. A crystalline trihydric alcohol has been isolated from Artemisia absinthium L.[12], which



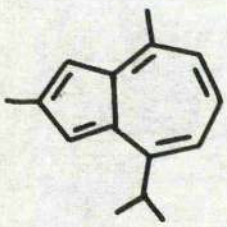
(9)



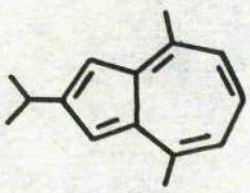
(10)

yields artemazulene (10) on dehydration and dehydrogenation[13].

Zierazulene (11) is obtained from Zierone after dehydrogenation[14]. It is



(11)



(12)

of interest that in this azulene the normal head to tail linkage of one of the isoprene units is reversed, but this is

thought to be due to methyl group migration[14].

Vetivazulene (12) may be isolated from Vetiveria Zizanioides[15], and is the only azulene to have been reported in animal matter. Prelog & Vaterlaus[16] isolated it from the neutral lipid fraction of pregnant mares' urine in a concentration of about 10^{-7} gms. per litre.

Azulene itself has been reported in tobacco smoke[17], and has been isolated from caucal oil[18].

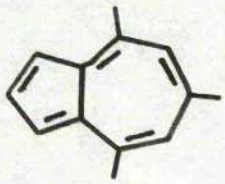
Numerous claims have been advanced for pharmacological effects of azulenes. Among recent examples are claims for antiphlogistic and antiallergic action[19], and antiarthritic, bacteriostatic, and cancerostatic action[20].

However, the evidence is conflicting, and little work appears to have been done using adequately purified azulene samples, and sound statistical techniques.

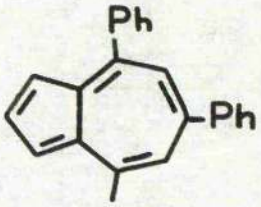
AIII Azulenes: Isolation and Purification

In common with most aromatic hydrocarbons, most azulenes form crystalline complexes with the usual reagents. The azulenes can readily be regenerated by chromatography on alumina[2,5]. Little success has attended attempts to separate individual azulenes by fractional crystallisation of the complexes[21,22,23], and mixed melting points of the complexes of different azulenes do not always show a depression[24].

Steam distillation may be used for the purification of low molecular weight azulenes, e.g. 4,6,8-trimethylazulene (13) (DV4). Azulenes



(13)



(14)

with higher molecular weight, e.g. (14), however, are too involatile.

Acid extraction, as first used by Sherndal[3], provides a convenient method for separating azulenes from non-basic contaminants. Some substituted azulenes, e.g. (14), however, suffer considerable decomposition under these conditions.

Alkylation of the azulene nucleus produces significant variations in its basicity, and this has been used as a criterion of identity. The distribution coefficient of an azulene between an organic phase and strong acid of known concentration provides a measure of the basicity[9,25,26]. This property has been utilised in conjunction with the Craig counter-current technique for separating azulenes, but results were not satisfactory[e.g.,22].

Chromatography of various kinds can be applied to azulenes. Adsorption chromatography is best performed on activated alumina. Azulene hydrocarbons are eluted by petroleum ether, and may be separated easily from azulenes containing polar substituents (e.g. acylazulenes), which are more strongly adsorbed. They may also be separated from non-

polar aromatic compounds and saturated or unsaturated aliphatic hydrocarbons. Among the azulene hydrocarbons, only a partial separation of alkylated azulenes can be achieved[27], unless very high adsorbent : azulene ratios are used[22]. Benzazulenes can be separated from alkylazulenes because the former are more strongly adsorbed.

Paper chromatography has been successfully used for identifying small quantities of azulenes, using paper impregnated with vaseline, and 40-70% phosphoric acid as the mobile phase[28,29,30].

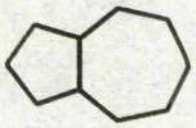
Very little data on the application of gas-liquid chromatography to azulenes has been published. A preliminary report[31] mentions that the ratio of retention volumes of azulene : naphthalene on a non-polar stationary phase at 200° is 1.8. The author's work (see appendix) shows that alkylated azulenes of different molecular weights can be separated efficiently by this method. On a preparative scale, gas-chromatography could provide a solution to such hitherto intractable problems as obtaining a clean separation of 1-methylazulene from azulene.

AIV Azulenes: Synthetic Routes to

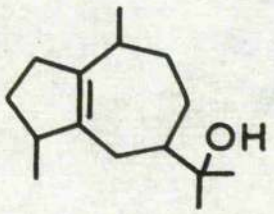
Methods for preparing azulenes may be divided into two classes; methods which involve a high temperature dehydrogenation, and non-dehydrogenative methods.

AIV1 Classical Syntheses of Azulenes

The earlier syntheses usually involved construction of the cyclopentanocycloheptane skeleton (15) in various stages of dehydrogenation.



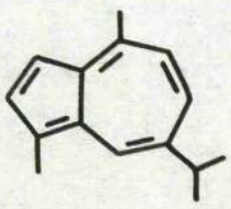
(15)



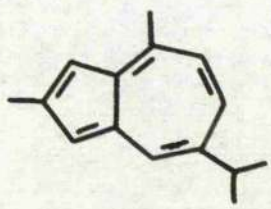
(5)

Dehydrogenation to the fully aromatic state is usually effected between 180° and 300° by palladium-charcoal, sulphur, selenium, or, recently[32] by PhS. radicals. These methods have been reviewed by Plattner[33].

The main disadvantages of this procedure are, (i) the yields are generally low (1-10%). In certain favourable cases, high yields may be obtained by catalytic dehydrogenation in the gas phase[34], but experimental conditions are highly critical. (ii) When applied to alkylated azulenes, group migration may occur. Thus, in the dehydrogenation of guaiol (5), two azulenes could be obtained[35], which were later shown to be (16) and (17)[36,37], depending on the temperature used for dehydrogenation.

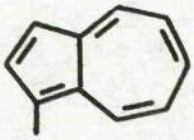


(16)

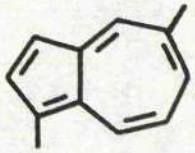


(17)

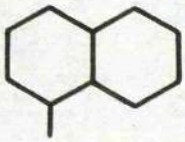
Subsequent work[38] suggested that migration occurs on the azulene nucleus, after dehydrogenation. Similarly a phenyl group was found[38] to be subject to migration between the 1- and 2-positions. The 2-position is preferred, presumably for steric reasons. (iii) Rearrangement of the azulene to the naphthalene nucleus takes place slowly at high temperatures (250-350°)[39]. The reverse of this can also occur. Thus 1-methylazulene (18) and 1,5-dimethylazulene (19) have been obtained by gas phase dehydrogenation of 1-methyldecalin (20) and 2,6-dimethyldecalin (21) at high temperatures[40].



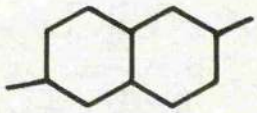
(18)



(19)

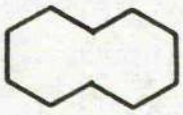


(20)

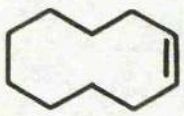


(21)

Azulene may be obtained directly from the cyclodecane skeleton by transannular dehydrogenation. Thus cyclodecane (22) and cyclodecene (23) have been reported to give yields of azulene as high as 50% and 70% respectively, by catalytic gas-phase dehydrogenation[41].

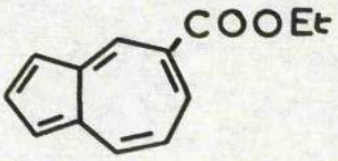


(22)

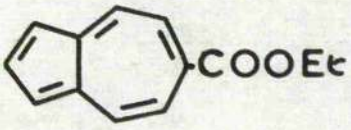


(23)

The required 0:3:5-bicyclodecane system, e.g. (15), can be obtained by normal procedures. Ring expansion of indanes by ethyl diazoacetate was used by Plattner and Wyss[42] to prepare 1- and 2-methylazulene, 1,2-dimethylazulene, and 4,8-dimethylazulene, and has been widely used since. A disadvantage of the method is the ambiguity involved in syntheses of 5(7)-substituted azulenes, since ethyl diazoacetate can add in two ways to indane. This was elegantly demonstrated by the formation of both 5- and 6-azulenecarbethoxylates (24) and (25), by the action of ethyl diazoacetate on indane, and by carrying out the catalytic dehydrogenation before hydrolysis of the ester functions. The two products (24) and (25) can in this case be separated easily, by



(24)



(25)

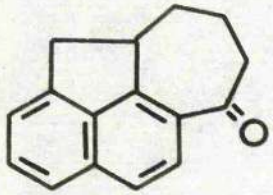
the considerable difference in their saponification rates[43].

The Demjanov ring expansion procedure has been used on the appropriate aminomethyl indanes. It was first applied to azulene synthesis by Arnold[44], who attempted to prepare 6-methylazulene, which is inaccessible by the ethyl diazoacetate method, but the result was a mixture of 5- and 6-methylazulene.

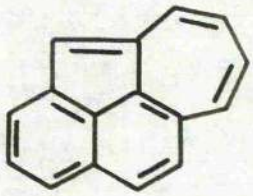
Diazomethane has also been used for the ring expansion

of indane and its derivatives at low temperature by irradiation with ultra-violet light[45].

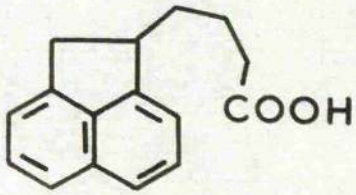
The 0:3:5-bicyclodecane skeleton may be constructed by cyclisation of a substituted cyclopentane ring. This method is particularly suitable for some annellated azulenes where the cyclisation required is onto an aromatic nucleus. Thus, the skeleton (26) required for the azulene (27), is readily accessible through phosphoric acid cyclisation of the acid (28)[46].



(26)

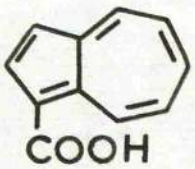


(27)

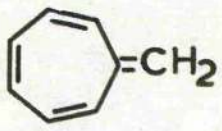


(28)

Conversely, a cyclopentane ring may be fused onto a preformed cycloheptane ring. Thus, the first synthesis of 1-methylazuloate (29) had, as its first step, the condensation of cycloheptanone with methyl succinate[47].



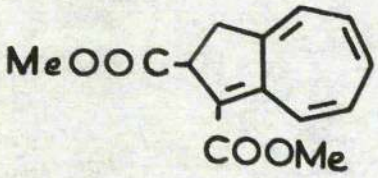
(29)



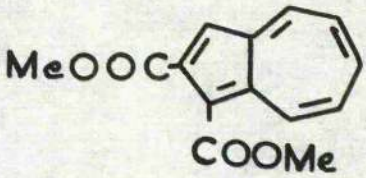
(30)

An interesting recent example in this category is the action of acetylene dimethylcarboxylate on cycloheptafulvene (30), which results in the dihydroazulene (31). Air oxidation

sufficed in this case for dehydrogenation to the azulene (32)[48].



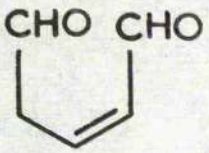
(31)



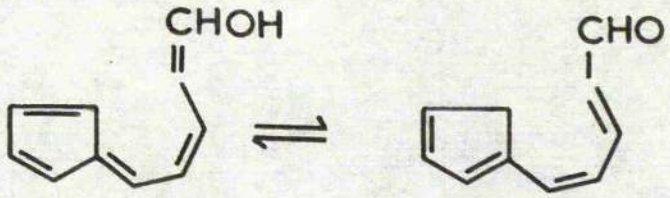
(32)

AIV2 Azulene Syntheses: Non-Dehydrogenative Methods

A convenient azulene synthesis from cyclopentadiene was reported independently from two laboratories[49,50]. Formally, this involves the condensation of glutacondialdehyde (33) with cyclopentadiene to give the fulvene aldehyde (34), and subsequently, by further condensation, azulene (1).

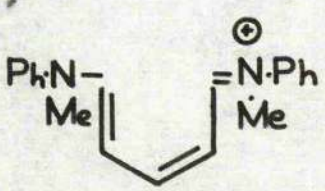


(33)

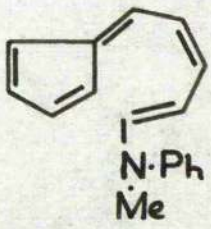


(34)

The direct condensation with glutacondialdehyde has not been achieved, but the anil (35) readily condenses with cyclopentadiene to give the fulvene (36), which cyclises to azulene when heated in vacuo, or treated with superheated steam. Yields are of the order of 60%. The anil (35) was obtained from (37)

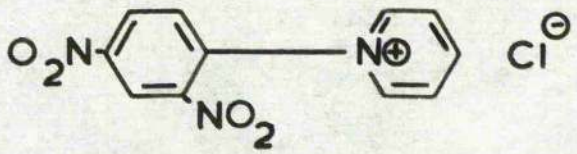


(35)



(36)

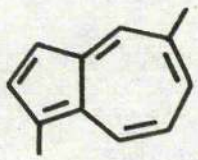
by cleavage of the pyridine ring in the presence of N-methylaniline.



(37)

Subsequent improvements to the procedure have been the preparation of the anil (35) by the interaction of cyanogen bromide with N-methylaniline and pyridine[51], and the use of benzidine[52], and, later, triethanolamine[53] for the cyclisation of the fulvene (36).

Various substituted azulenes may be prepared by this method. If a monoalkylcyclopentadiene is used, 1-alkylazulene is the only product[52]. Indene gives 1,2-benzazulene[51]. Substituted pyridines afford azulenes with substituents in the seven-membered ring, although it must be borne in mind that ambiguity is possible in certain cases. 1,5-Dimethylazulene (19), for instance, cannot be unequivocally synthesised by this method. 6-Benzylazulene has been



(19)

prepared from a benzyl derivative of (35), starting with 4-benzylpyridine and cyanogen bromide[54]. This method failed for 5-benzylazulene, however, as the corresponding anil from

m-benzylpyridine could not be isolated[54].

Two variations of this method have been published, involving condensation of metal cyclopentadienides with N-alkylpyridinium salts[51] and pyrylium salts[55,56] respectively. It is proposed[56] that the pyrylium salt (and, analogously, the N-alkylpyridinium salt) suffers nucleophilic attack by the cyclopentadienide anion at the 2- or 4-position. The product from attack at the 2- position yields an azulene by tautomeric rearrangement and subsequent elimination of water (or an amine) as depicted in Fig. 1

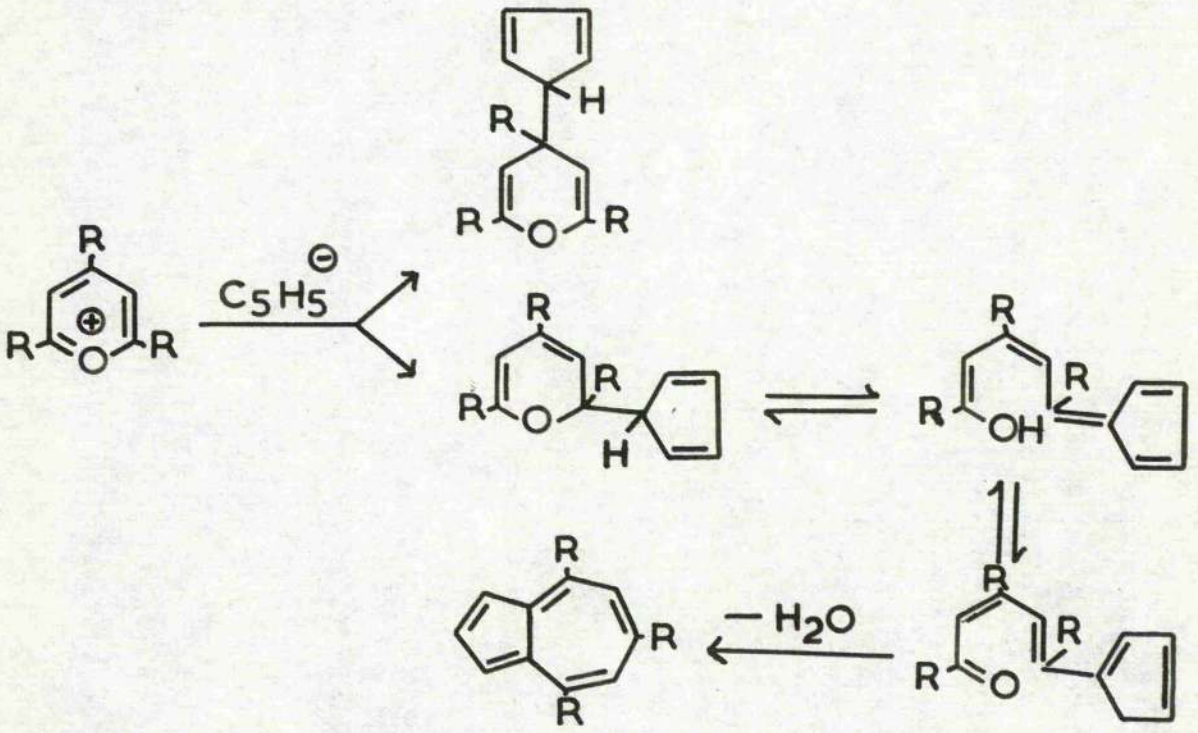


Fig. 1

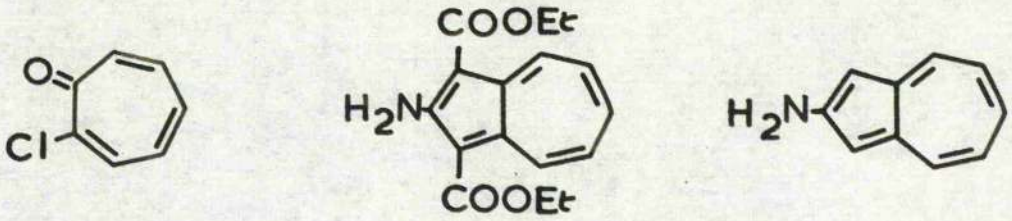
A strong base such as potassium tert. butoxide is sometimes,

but not always, necessary to liberate the free azulene.

This method is inapplicable to azulene itself, as substituents appear to be necessary in the 2-, 4-, and 6-positions of the pyrylium salt. The yield of azulene is also sensitive to the size of the 4- and 8- substituents, the best results being obtained for a 4,8-dimethylazulene. Replacement of one of these methyl groups by phenyl reduced the yield considerably[56], and no azulenic product was obtained from 2,4,6-triphenylpyrylium perchlorate[56] or 2,6-ditertiarybutyl-4-methylpyrylium perchlorate (DXXI). The use of monomethylcyclopentadiene gives the corresponding 2-methylazulene[56], which contrasts with its behaviour with the anil (35)[52], and is no doubt due to the steric influence of the 4- and 8- substituents.

It is thus seen that this is a more limited method for azulene preparation, but it has the considerable advantage, when applicable to azulenes with heat sensitive substituents, that reaction is best carried out at low temperatures (-20°). In favourable cases the yields are high, and the author has prepared 4,6,8-trimethylazulene is this way in > 90% yield (DV).

Complementary methods, which start from a preformed cycloheptatriene ring have been developed by Nozoe and coworkers[57]. As an example, when a mixture of 2-chlorotropone (38) and two or three equivalents of cyanoacetic ester are allowed to stand in ethanolic solution



(38) (39) (40)

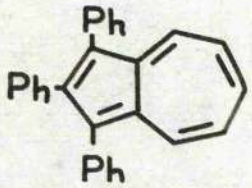
for a few hours at room temperature, the azulene (39) is formed as the main product, which can easily be isolated as orange-yellow crystals in 70% yield. The carbethoxyl groups may be removed successively by hydrolysis and decarboxylation, resulting in 2-aminoazulene (40). The 2-amino group can be removed by the Griess deamination procedure, or it can be replaced by other groups by Sandmeyer reactions. This indicates the particular promise for this method, in providing a convenient route to the 2- substituted azulenes. The technique has been applied to substituted 2-halogenotropones, and to the preparation of azulenes containing a heteroatom in the skeleton[57]. The main disadvantage of the method at present is the relative inaccessibility of the tropone derivatives used as starting materials.

AIV3 Miscellaneous Preparations of Azulenes

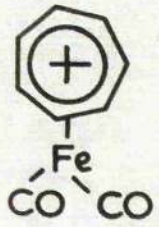
Azulene formation occurs in several diverse reactions, although, as a rule, these are of little use as preparative methods.

Dimerisation of 1,2-diphenylacetylene in the presence of 2,4-dinitrobenzenesulphonyl chloride and aluminium chloride gives 1,2,3-triphenylazulene (41) in 25% yield[58]. This

structure (41) was confirmed by an independent fourteen stage synthesis starting from cycloheptanone[59]. The reaction is of



(41)



(42)

interest in being the first recorded example of the expansion of a benzene ring to a seven-membered ring under ionising conditions.

Azulene is formed in low yield during the preparation of cyclooctatetraene by cyclopolymerisation of acetylene[60]. It is also formed as a by-product in the commercial manufacture of acetylene itself[61].

The dicarbonyltropyliumiron cation (42), when treated with a metal cyclopentadienide, yields an azulene. The structure of this has not been elucidated, but it is thought to contain a 3-carbon side chain[62].

AV Azulenes: Spectra

A characteristic property of the azulene nucleus, in contradistinction to naphthalene, is its electronic transition in the long wave region, which results in its deep blue colour. It has been argued that the fact that azulene is best represented as having contributions from dipolar forms (see AVI) affords an explanation of the colour. Heilbronner, on the

other hand, has deduced the existence of the long wave transition from a simple valence bond model based on apolar limiting structures, and has argued that the colour is primarily a consequence of the particular topology of azulene[63].

Whereas alkylation in any position of naphthalene produces a bathochromic shift of the longest wavelength absorption bands, this effect only occurs at the 1(3)- and 5(7)- positions of azulene. A hypsochromic shift is associated with substitution in the remaining 2-, 4(8)-, and 6- positions[8]. Only the visible band is thus affected, for the ultra-violet band suffers normal bathochromic translation for substitution in all positions, although the magnitude of the shift varies[64].

It was shown[8] that polysubstitution of the azulene nucleus by alkyl groups causes shifts which satisfy simple additivity rules. The mean displacement of λ max. associated with each position is shown in Fig. 2. The shift is independent of the size of the alkyl group. The values of $\Delta\lambda$ max. are usually

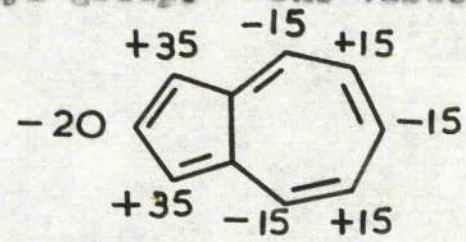


Fig. 2. Average displacements of λ max. (m.μ.) associated with alkylation of each position of azulene.

calculated from the longest wavelength absorption peak, but this is not always easy to define in the highly alkylated azulenes, where fine structure may be lacking. $\Delta\nu$ max.

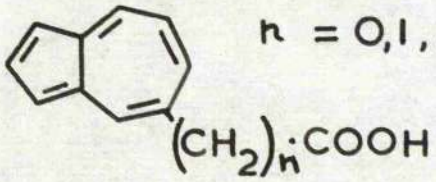
Values are practically independent of the maxima from which they have been measured, whereas $\Delta\lambda$ max. values are not, since a distortion is introduced by the relation $\lambda = 1/\nu$. Thus for comparative purposes $\Delta\nu$ max. is the more useful quantity, and it may be calculated from the absolute maxima.

These results, known as the "Plattner rules" have been a valuable aid to determining the orientation of unknown alkylated azulenes. Heilbronner[65] analysed the data for about 50 alkylated azulenes by normal arithmetical procedures, and concluded that the standard error for individual predictions by additivity is $\pm 90 cm.^{-1}$ which corresponds to about ± 3 m.μ., depending on the absolute position of the maximum. Hence, on a significance level of 95%, a deviation of more than 180 $cm.^{-1}$ or 6 m.μ. between observation and theory is significant, and suggests either that the proposed structure is wrong, or that some other effect, such as steric interference, is operative. The displacements are predicted reasonably well by an L.C.A.O. - Molecular Orbital treatment of azulene, providing that the peturbations due to both the inductive and the hyperconjugative effects of the alkyl groups are taken into account[66].

Electron attracting groups, such as carboxyl, carbethoxyl [47,67,68] or aldehyde[69,70,71,72], have the opposite effect. A series of fifteen 1-formylazulenes, prepared by the action of dimethylformamide and phosphorus oxychloride on the corresponding azulenes, all showed a hypsochromic displacement

of λ max. (cyclohexane) of between 22 and 43 m.μ. , relative to the unformylated azulene nuclei[72].

A demonstration of the insulating effect of methylene groups has been given by Treibs[73], who prepared, and determined the spectra of, the four compounds (43). When $n \geqslant 2$ the group functions, spectrally, as an alkyl substituent, and it is



(43)

suggested that this effect may be used to assess inductive effects and their transmission.

When the substituent (e.g. phenyl) is able to conjugate with the azulene nucleus, the mesomeric effect assumes greater importance than the inductive effect. From spectral determinations recorded in the literature for the five phenylazulenes[74,38,75,76,77], it appears that all except 2-phenylazulene (λmax. 578[38]) suffer a bathochromic shift. The position is complicated, however, by the possibility of steric interference. On the assumption of interference radii of hydrogen atoms as proposed by Braude[78], both 1- and 4-phenylazulene must be forced out of co-planarity. This is reflected in the abnormal melting points for these two compounds, and in the tendency for 1-phenylazulene to rearrange to 2-phenylazulene[38]. When steric interactions occur, the

spectra do not generally conform to additivity rules. An example of this is 1,2,3-triphenylazulene (41)[58]. The position of its absorption maximum (C. 605 m.μ.) is not where it might be expected (630 m.μ.) on the basis of 1-phenylazulene (λmax. 606[74]$_{m\mu}$) and 2-phenylazulene (λmax. 578[38]$_{m\mu}$), for the 2-phenyl group is probably forced out of co-planarity by the 1- and 3- phenyl groups.

AVI The Relationship of Azulene to other Carbocyclic Systems

Opinions have varied as to whether azulenes should be classed as aromatic or as olefinic compounds. Sherndal[3] concluded that they are aromatic, since they form complexes with picric acid, and sym-trinitrobenzene etc., but subsequent evidence was conflicting. Aromaticity is indicated by the facts (i) that azulenes are formed by dehydrogenation at high temperatures, (ii) that they are reversibly soluble in acids, and (iii) that they react by substitution with mild electrophilic and nucleophilic reagents. Azulene also possesses the considerable resonance energy of 47 k. cal./mole., based on heats of combustion[79]. On the other hand they can be reduced catalytically, and are degraded by oxidising agents such as ozone, alkaline potassium permanganate[4], and nitric acid[80]. Vigorous reactions take place with bromine or nitrosyl chloride, but no well defined products are obtained[80]. Azulene can be thermally rearranged to its isomer naphthalene[39], and, as recently as 1950, Pommer[81]

concluded from data of this kind that azulene was not aromatic.

The difficulty, of course, stems from the lack of a satisfactory definition of aromaticity. Originally the term was applied to all compounds having a pleasant smell or taste. When Kekulé[82] proposed the well known conjugated cyclic structure for benzene, he suggested that the presence of this nucleus should be a necessary and sufficient condition for a compound to be classed as aromatic, but a few months later Erlenmeyer[83] proposed that the definition of aromaticity should again be based on a similarity of properties rather than a common structural feature, although at the time the properties in question were associated with a single structural type. This is still essentially the view held today.

It is generally agreed that the distinguishing feature of aromatic compounds is their considerable stability. Consequently they have a relatively high resonance energy, and they tend to react by substitution rather than addition, and retain the structural nucleus.

From the point of view of classifying compounds, these criteria suffer from the disadvantage that they are quantitative, and it is necessary to draw an arbitrary dividing line across a series which may have a continuous gradation of properties. However, there is no a priori reason why aromaticity should be a discontinuous property, but a better elucidation of the

structural (electronic) factors which determine aromaticity is desirable. So far attempts in this direction have met with partial success.

An empirical thermodynamic definition has been proposed by Dewar[84]. This defines an aromatic compound as one "with a large resonance energy, where all the annular atoms take part in a single conjugated system". This does little to advance understanding of the phenomenon, but it is perhaps the most useful working definition that can be devised at present, for it is not usually considered within the province of the chemist to enquire too closely into the ultimate nature of reality.

An interesting recent suggestion[85] is that a quantitative definition should be formulated in terms of proton chemical shifts. An aromatic compound might thus be defined as one which will sustain an induced ring current.

The concept of the now famous "aromatic sextet" was the first notable advance in the attempts to rationalise aromatic phenomena in terms of electronic theory[86]. This proposed that the association of 6 π valency electrons in a conjugated cyclic system conferred a particular chemical stability upon the system. Its most notable success has been in its application to benzene, and the ions of cyclopentadiene and cycloheptatriene.

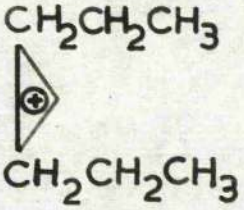
Later it was recognised that the stability of the aromatic sextet exemplifies a more general truth, when Hückel

developed his rule that aromatic character will be shown by conjugated carbocyclic rings having $(4n + 2)\ \pi$ electrons where n = o, 1, 2 ... [87]. Hückel extended the ideas of valence bond and molecular orbital approximation, which had been largely developed by Pauling[88] and Coulson[89] respectively, and showed that the binding energies of molecular orbitals in cyclic systems will be at a maximum in rings with $(4n + 2)\ \pi$ electrons. The π electron system will also be unusually stable by virtue of the fully filled molecular orbitals with considerable delocalisation energy if the rings are planar.

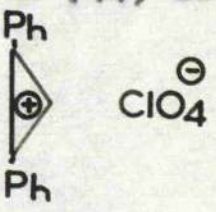
The predictions of this theory are borne out moderately well in practice for monocyclic systems, and in many cases, though without formal proof, to polycyclic systems.

The simplest series of compounds embraced by the Hückel rule, those with two π electrons (i.e. n = o), was shown to have a stable member (apart from the special case of the double bond) by the isolation of the sym-triphenylcyclopropenylium cation (44)[90]. That the stability of this cation (44) is not

(44)



(45)

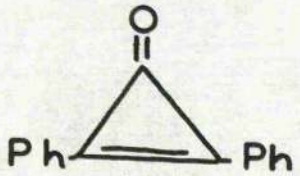


(46)

accounted for by the phenyl groups was proved by the preparation of (45) as a stable perchlorate[91]. A comparison of this with diphenylcyclopropenylium perchlorate (46)[92], indicates

that the phenyl groups do not stabilise the cation more than alkyl groups do. This is because they stabilise the covalent cyclopropene even more than they stabilise the cyclopropenylium cation[91].

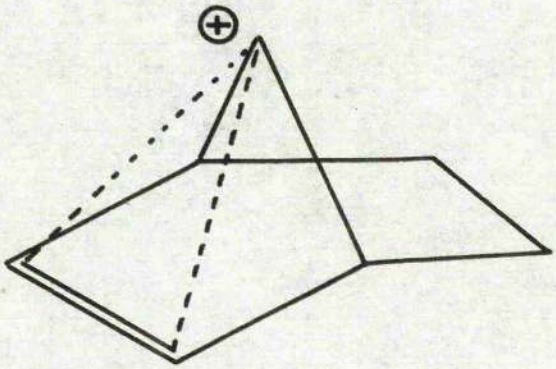
The anion, $Ph_3C_3^-$, corresponding to (44), has been synthesised as an unstable intermediate[93], and also the radical $Ph_3C_3^{\bullet}$, which yields a dimer and rearranges to hexaphenylbenzene[94]. It is thus in accordance with Hückel's rule that only the cation (44) of these three should be stable. Diphenylcyclopropenone (47) has also been synthesised[95,96]. This ketone is of interest because it bears the same relationship to the cyclopropenylium cation of (46) as tropone does to



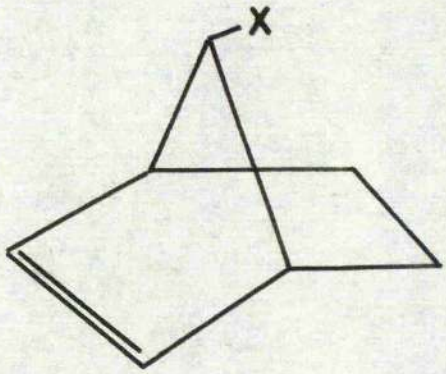
(47)

the tropylium ion, and is therefore expected to show some aromatic properties. Diphenylcyclopropenone (47) decomposes at 130-140°, yielding diphenylacetylene and carbon monoxide. This comparatively high temperature of decomposition, and the fact that it can be isolated from a hydroxylic medium, indicates that the system must have a large resonance stabilisation, especially so since there must be high angle strain.

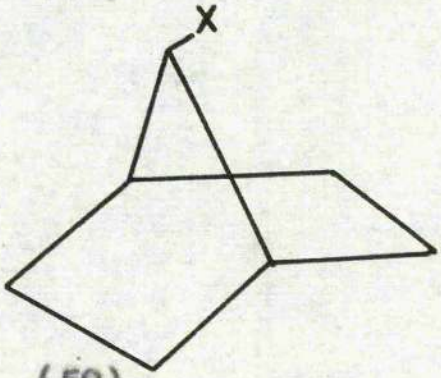
Another demonstration of the stability of the two electron system is given by the 7-norbornenyl cation (48). The anti-7-norbornenyl derivative (49) (x = p-toluenesulphonyl)



(48)



(49)



(50)

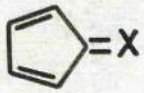
is more reactive than the related 7-norbornyl derivative (50), in acetolysis, by a factor of 10^{11}. This is attributed to the high stabilisation of the cation (48) by non-classical electron delocalisation as shown.[97]

The next member of the series which has $(4n + 2)\ \pi$ electrons is the group of compounds with $6\ \pi$ electrons ($n = 1$). Benzene is the foremost example, and was the first aromatic compound to be discovered. Its properties are well known. Its stability is enhanced by the fact that the geometry of the molecule does not necessitate angle strain in the planar

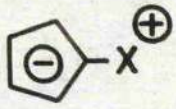
state.

Of the four possible singly charged ions derived from cyclopentadiene and cycloheptatriene, the Hückel Rule predicts that two of them, the cyclopentadienide anion and the cycloheptatrienylium cation, should show aromatic properties, and this is in fact the case.

Thiele[98] first described the formation of the cyclopentadienide anion when he prepared potassium cyclopentadienide. Later it was realised that the acidity of cyclopentadiene is connected with the possibility of developing a sextet of electrons in the anion[99]. The tendency for this system to develop plays an important part in the stability of cyclopentadiene derivatives (e.g. (51)) having an extracyclic double bond, providing that the electronegativity of the atom



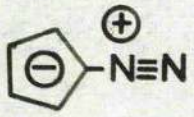
(51a)



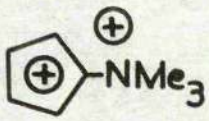
(51b)

or group X is such that polarisation in the sense of (51b) is possible. An interesting example of this is fulvene ((51), X = CH_2). This has been known for some time as an unstable yellow oil[100], and this has now been purified in quantity, and its properties studied[101]. It shows both definic and some aromatic properties. The most remarkable fact about it is its dipole moment, which is as high as 1.1 D. This reflects the great tendency for formation of the

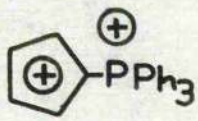
cyclopentadienide anion. Compounds which are analogous, although uncharged canonical structures cannot be written for all of them, are ones with an ylide structure. The simplest examples are diazocyclopentadiene (52),[102] trimethylammonium-cyclopentadienylide (53)[103], and triphenylphosphoniumcyclo-pentadienylide (54)[104,105], all of which show aromatic stability. The formation of a negatively charged five membered



(52)



(53)



(54)

ring was postulated early on to account for the aromaticity and deep colour of the anhydronium bases[106,86].

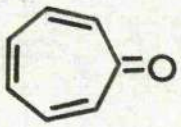
In compounds of type (51) where X is a strongly electronegative atom, e.g. oxygen, stability is less than that of cyclopentadiene. Cyclopentadienone is too unstable to exist, and at least two aryl substituents are necessary, with bulky groups in both positions adjacent to the carbonyl group, to allow isolation of the ketone[107]. (C.f. Ease of formation of tropone).

When cyclopentadienide ions are treated with ferrous ions[108], they yield the completely covalent neutral molecule dicyclopentadienyliron or ferrocene, in which all the carbon-hydrogen bonds are equivalent and the two five-membered rings are planar and symmetrical. Its properties suggest that its

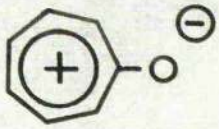
aromatic stability is of a higher order than that of benzene itself[108,109,110,111,112].

The other ion relevant to this discussion, the cation of cycloheptatriene (55), was probably first prepared as the bromide in 1891[113]. Later[114] it was recognised that although

(55)



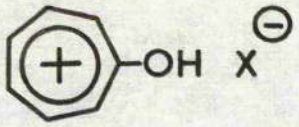
(56a)



(56b)

the carbon bromine bond normally tends to be covalent, the delocalisation energy of the cyclic ion is sufficient to overcome this and endow cycloheptatrienylium bromide with a salt-like structure.

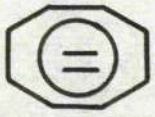
Significantly, cycloheptatrienone, or tropone (56), presents no difficulties in its synthesis[115]. In this case the normal polarisability of the carbonyl group is complementary to the requirements of the ring for developing an aromatic sextet, so that the canonical form (56b) makes an important contribution to its ground state. This is reflected by the ready formation of a stable series of salts of the hydroxy-cycloheptatrienylium cation (57) on treatment with acids[116], its large dipole moment (4.3D)[116], and its abnormally low carbonyl stretching frequency (1638 cm.$^{-1}$)[115]. This contrasts with the failure to isolate cyclopentadienone[107], and is in complete accordance with Hückel's Rule.



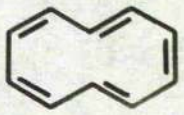
(57)

Cyclobutadiene, with 4π electrons, is intermediate between the 2 and 6π electron systems, and so according to Hückel's Rule should not show aromatic stability. After many fruitless attempts it has probably been formed, as a gas, with a half-life of about one minute[117].

Only one monocyclic structure with 10 π electrons ($n = 2$) has been prepared. This is the cyclooctatetraenyl dianion (58) which was obtained by the action of potassium on cyclooctatetraene. The compound was not isolated, however,



(58)



(59)

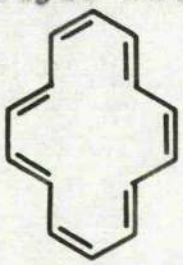
and evidence for its existence is based mainly on the proton magnetic resonance spectrum[118]. Although the unknown cyclodecapentaene (59) should exhibit aromatic character by virtue of its $(4n + 2)\ \pi$ electrons, the molecule would be subject to "H inside" interference. Thus if a scale drawing of the molecule is constructed in which 120° angles are assigned between all the valence bonds, then two of the hydrogen atoms disposed towards the centre of the ring will be found to be subject to mutual steric interference. The strain in system (59) may therefore be out of proportion to the resonance energy

which would be developed by assumption of the planar state.

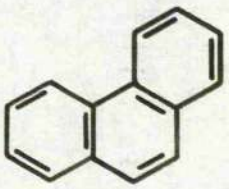
If Hückel's Rule is applied to polycyclic systems, for which there is no theoretical justification, but some empirical support, then both azulene and naphthalene may be regarded as 10 π electron systems with peripheral conjugation.

Again, the intermediate systems (7, 8, and 9 π electrons) have no known members which show aromatic properties. Cyclooctatetraene is definic in its properties[119]. Both cyclooctatetraene and cyclobutadiene could, hypothetically, give rise to both stable anions and cations.

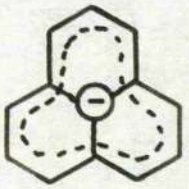
Cyclotetradecaheptaene (60) (14 π electrons: n = 3) has been described[120]. It is non-planar and unstable, being destroyed after standing in light and air for one day.



(60)



(61)

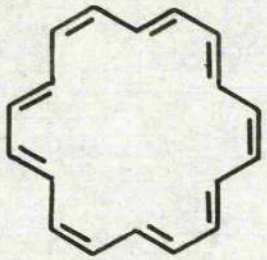


(62)

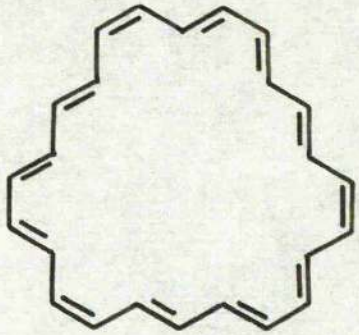
Phenanthrene (61), and the perinaphthyl anion (62) are polycyclic examples of this system. The latter structure is interesting, for in spite of the Hückel Rule, both the corresponding cation and radical are of comparable stability[121].

Some properties of cyclooctadecanonaene (63) which has 18 π electrons (n = 4) have been described[122,123]. It appears to be more stable than cyclotetracosadodecaene (64) which decomposes on exposure to air or sunlight[123], but it does not

have any marked aromatic stability. The latter possesses 24 π electrons and so is not embraced by Hückel's Rule.



(63)



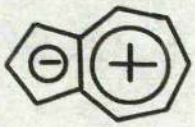
(64)

Mislow[124] has concluded, from scale drawings, that cyclopolyolefins up to $C_{28}H_{28}$ must assume a buckled rather than a planar configuration by virtue of steric interference. In this case cyclotricontapentadecaene ($C_{30}H_{30}$) would be the first large ring embraced by the Hückel Rule which could assume the planar state with little strain. This has recently been synthesised however, and it is unstable. It is destroyed by air or light after several hours, and decomposes in a dilute benzene or dioxan solution kept at room temperature[125]. This is the largest relevant cyclic compound so far synthesised. It thus appears that although the Hückel Rule is useful for the compounds with less than 14 π electrons, its predictions for larger systems are not well verified.

A logical extension of the foregoing idea, that there are certain preferred electron groupings, analogous to the stable shells of electrons associated with atomic nuclei, is the idea of molecules in which such a system may develop by an overall polarisation. This was discussed earlier with

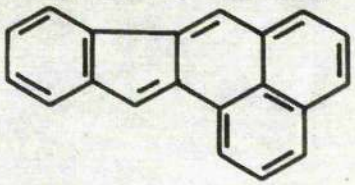
reference to the aromatic properties manifested by five and seven-membered rings.

A further possibility is a molecule where two complementary stable π electron systems may develop by an overall polarisation. It was suggested[126,127] that dipolar forms, e.g. (1d), might contribute to the ground state of azulene as resonance hybrids. However, its small dipole moment (1 + 0.05 D[128]) shows that

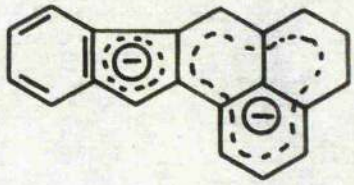


(1d)

the extent of polarisation in the ground state must be small. One other carbocyclic compound of this type has been synthesised, viz. (65)[129], in which the stability of the perinaphenylium cation is complementary to that of the cyclopentadienide anion.



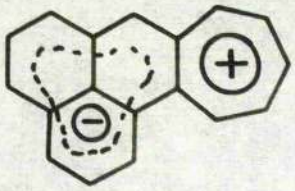
(65a)



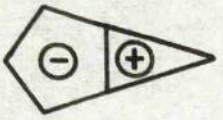
(65b)

Some other hypothetical compounds which would be of interest for this reason are indicated by the limiting structures (66) - (70) inclusive.

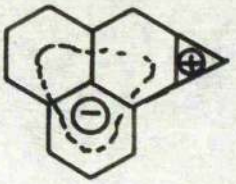
Chemical evidence suggests that azulene possesses a degree of aromaticity which is intermediate between the benzenoid hydrocarbons and the polyolefins, and there are two ways of interpreting its aromaticity in terms of Hückel's theory.



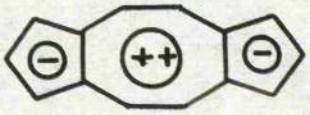
(66)



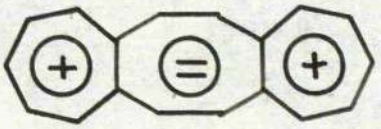
(67)



(68)



(69)



(70)

That is, either as a 10 π electron system, or as two complementary sextets.

If it is regarded as a 10 π electron system in which there is complete peripheral delocalisation, then it represents cyclodecapentaene, in which the problem of internal steric interference has been obviated by a trans-annular valency bridge. In contrast to its isomer naphthalene, neither of the Kekulé forms which may be drawn for azulene have a double bridging bond. X-ray and electron diffraction studies[63] have indicated that whereas the mean length of the peripheral bond is about 1.39A°, the trans-annular bond seems to be somewhat longer, about 1.45A°.

This concept of azulene was first suggested[130] on the basis of a simplified molecular orbital treatment before much experimental evidence was available. The L.C.A.O. Molecular Orbital method[87] was first applied to azulene by Coulson and Longuet-Higgins[131], and by Brown[132], and with refinements by later workers[133,134]. Predictions by this method tend to

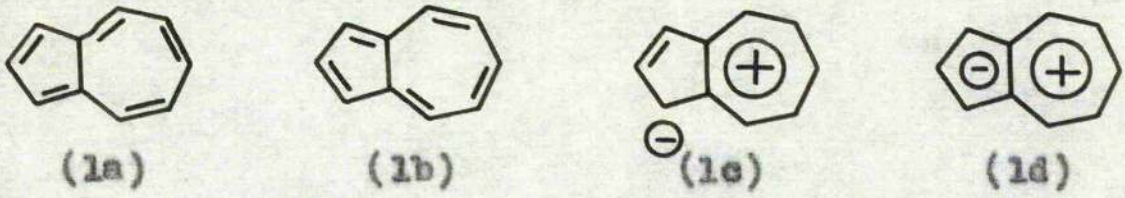
overestimate the dipole moment, but the positions of attack by electrophilic and nucleophilic reagents are successfully accounted for.

A useful simplification of the method of applying the Hückel L.C.A.O. - M.O. method derives from Dewar and Pettit's demonstration[135] that the properties of mesomeric hydrocarbons can be deduced from those of cyclic polyenes by treating the formation of cross-links as a perturbation. The application of this to azulene and naphthalene is discussed by Heilbronner[63], and, in a form generally applicable to non--alternant hydrocarbons, by Peters[136].

The important achievement of such a model is that it predicts the unique blue colour of azulene, although the predicted position of max. (460 m.μ.[63]) is in poor agreement with the observed position of 580 m.μ. It is also comparatively simple for purposes of calculation.

On the other hand, the trans-annular bond of azulene allows a π electron sextet to be developed in each ring by polarisation. Considering that the dipole moment of azulene is small (1.0 ± 0.05 D[128]), it is reasonable to formulate azulene as a resonance hybrid of mainly the two kekule forms (1a) and 1b), but with a small contribution from structures of type (1c) and (1d).

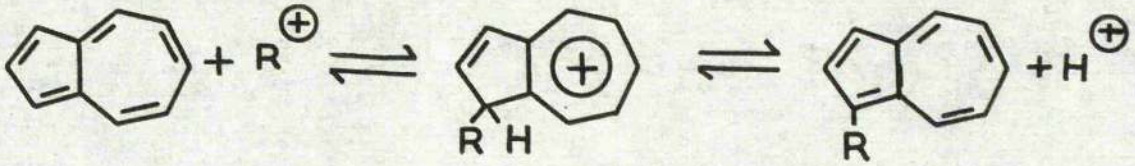
During reaction, the transition states are stabilised by the formation of a tropylium cation or a cyclopentadienide



(1a) (1b) (1c) (1d)

anion (see Fig. 3), and this accounts for the very mild conditions which are necessary to effect electrophilic or nucleophilic substitution.

Electrophilic Substitution:



Nucleophilic Substitution:

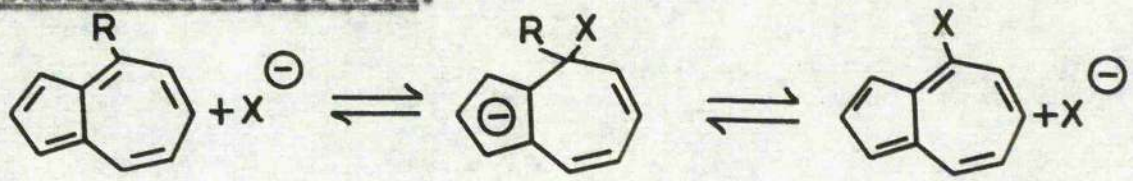
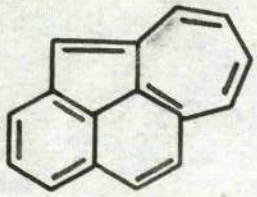
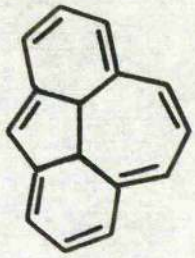


Fig. 3

An interesting experimental investigation into the importance of polarisability in the fine structure of azulene was an attempt to synthesise the two hydrocarbons (71) and (72)[46]. Inspection reveals that whereas cyclohepta(b,c)-acenaphthalene (71) may be represented as electronically independent naphthalene and azulene nuclei fused together, and various polar canonical forms are possible, it is not possible to draw a fully conjugated structure for (72) which does not involve a double bond across the 9-10 positions of the azulene skeleton. Only two polar forms with a negative

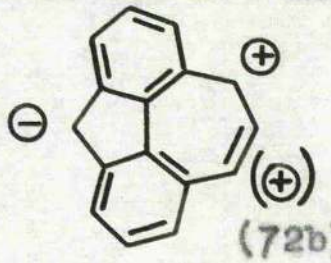


(71)



(72a)

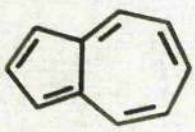
charge on the five-membered ring (at C_2 of the azulene skeleton) (72b) can be depicted. Hence, azulenic properties should be well developed in (71), but considerably attenuated in (72). The latter could not be isolated, as the corresponding dihydro ester did not undergo dehydrogenation, whereas (71)



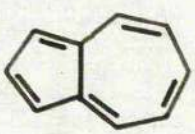
(72b)

was successfully synthesised, and shown to have a basicity of a high order for azulenes[46].

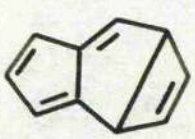
Quantum-mechanical valence bond models for azulene have been used, which are based on the two Kekulé structures (1a) and (1b), with appropriate contributions from the fifteen limiting structures, such as (1c), which have a single "long" bond[79,137]. These calculations predict that the long wave transition will be at 690 m.μ. (observed, 580 m.μ.). Their main fault, however, is that they predict a uniform charge distribution, with



(1a)



(1b)



(1c)

no dipole moment. The inclusion of polar limiting structures (see above), which affords a very good qualitative interpretation of the data, leads to very complex calculations if applied quantitatively[138].

To summarise; the most reasonable qualitative concept of azulene at present seems to imply that in the ground state it is essentially a cyclopolyolefin having ($4n + 2$; $n = 2$) π electrons, with a trans-annular single bond, which enables the molecule to assume a planar state. Under reacting conditions, the trans-annular bond becomes important in allowing development of a substituted vinyltropylium or cyclopentadienide structure. Both the ground state, and the transition state under electrophilic or nucleophilic attack, thus have stable π electron groups, and this accounts for the unusual chemical properties of the azulenes.

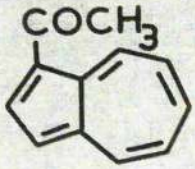
The innate tendency for the molecule to polarise, magnifies the effect of electron attracting or electron releasing substituents. The experimental results embodied in this thesis show that the electron releasing effect of alkyl substituents has a greater effect on the course of chemical reaction than is usually the case with benzenoid hydrocarbons.

AVII Azulenes: Electrophilic Substitution

AVII 1 Introduction

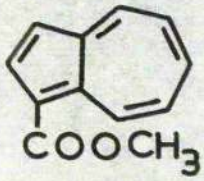
Calculation of the atom localisation energies for each

position of attack in azulene led to the prediction that electrophilic substitution should take place preferentially at position one[132]. This was subsequently confirmed by Anderson and co-workers,[139] who found that azulene with acid halides or anhydrides and aluminium or stannic chloride gives a mixture of the ketones (73) and (74), which can be separated



(73)

(74)



(29)

by chromatography. The ketone (73) was oxidised by sodium hypoiodite to azulene-1-carboxylic acid, which yielded 1-methylazuloate (29) on treatment with diazomethane. The ester (29) was independently synthesised[47] by the scheme outlined in Fig. 4., and the two products were shown to be identical. This was the first unequivocal proof that electrophilic substitution of azulene involved the 1(3)-positions.

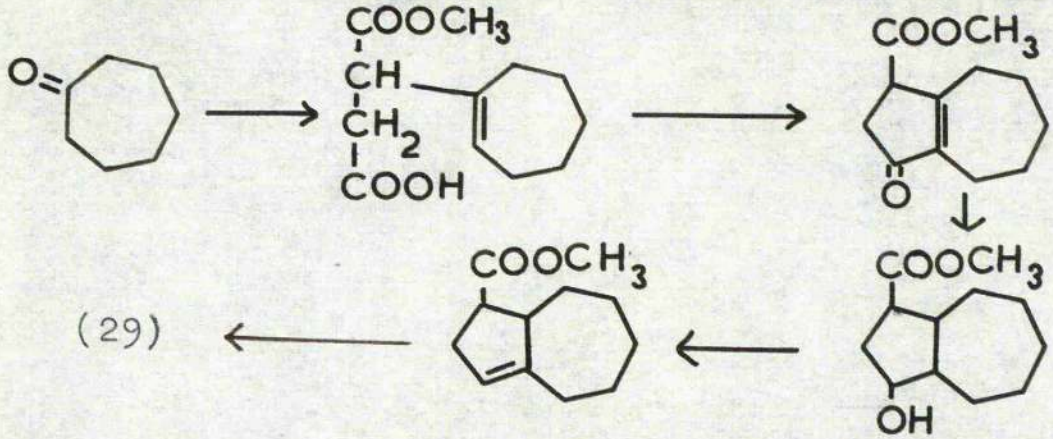
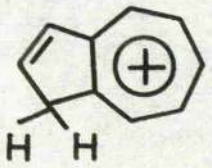


Fig. 4., Synthesis of 1-methylazuloate[47].

In accordance with the theories discussed in (AVI), very mild conditions usually suffice for electrophilic substitution of azulenes.

AVII 2 Protonation

The simplest form of electrophilic attack is protonation. It was therefore to be expected that when azulenes dissolve reversibly in strong acids[3], the addition of a proton would take place at the 1(3)-position[9]. A calculation of the delocalisation energies of all six possible azulenium cations, by the L.C.A.O. - molecular orbital approximation method, pointed to (75) as the most stable structure[140]. Recently, a study of the proton magnetic resonance spectrum of azulene



(75)

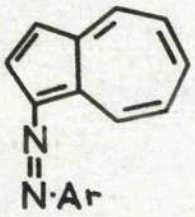
dissolved in trifluoracetic acid, and in carbon tetrachloride, confirmed this structure (75) experimentally, and further showed that the mean lifetime of the azulenium cation is of the order of one second[141]. When 4- and 8- methyl substituents are carried by the azulene nucleus, it is possible to isolate the corresponding cation as the crystalline perchlorate (CVII).

The visible spectra of azulenes dissolved in strong acids show a hypsochromic displacement of about 230 m.μ. relative to those in neutral solutions. This contrasts with the behaviour of benzenoid hydrocarbons. The spectra of azulenium

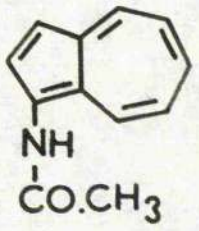
cations are useful for characterising individual azulenes.

AVII 3 Reaction of Azulenes with Aryldiazonium Salts

Azulenes with vacant 1(3)-positions couple easily with aryldiazonium salts, to give products which are exemplified by (76)[139,142,143,144]. This compound (76) can be reduced by sodium bisulphite to the unstable 1-aminoazulene, isolated as N-acetylaminoazulene (77)[143], which also results from the



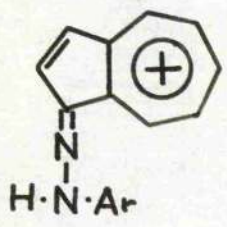
(76)



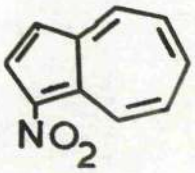
(77)

Beckmann rearrangement of the oxime of 1-acetylazulene[139], thus proving that aryldiazonium salts attack the 1-position.

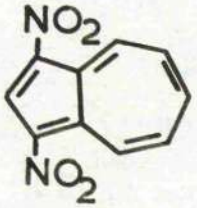
These arylazoazulenes appear to be more basic than the parent azulenes[142], and possess considerable dipole moments[145]. Protonation takes place preferentially at the nitrogen atom to the azulene nucleus, and results in cations of type (78)[144, 146,147].



(78)



(79)



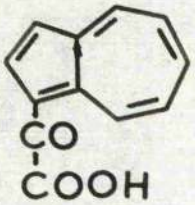
(80)

AVII 4 Nitration of Azulenes

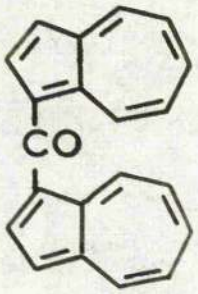
Nitration can usually be effected with cupric nitrate[139, 143], or, more generally, with tetranitromethane in pyridine at room temperature[143,148]. The reagents normally used for the benzenoid hydrocarbons, such as nitric acid[149], or a nitric acid-sulphuric acid mixture[143], fail with azulenes. Proof that (79) is the structure of the mono-nitration product of azulene was obtained by reductive acetylation to the known N-acetylaminoazulene (77)[139]. Azulene itself will also give 1,3-dinitroazulene (80).

AVII 5 Friedel-Craft Reactions on Azulenes

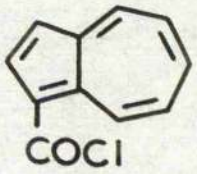
Only traces of alkylazulenes are obtainable from alkylhalides and azulenes[149], except in the case of 1-benzylazulene and 1-hexylazulene[27], but acid halides and anhydrides readily afford 1(3)-acylazulenes. It was later found[148] that in many cases catalysts are unnecessary. With oxalyl chloride at room temperature, azulene gives a mixture of azulene-1-glyoxylic acid (81) and di-1-azulenyl ketone (82). Guaiazulene behaves in a similar fashion. The proportions of these two types of product depends on the nature of the solvent employed. Using methylene chloride favours formation of the ketone (82), whereas in light-petroleum, production of the glyoxylic acid (81) prevails[148]. Oxalyl bromide with azulene gives azulene-1-glyoxylic acid (81), or, under more vigorous conditions, azulene-1-carboxylic acid[150,151].



(81)



(82)



(83)

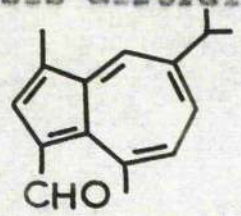
Various azulenes have been treated with phosgene to give 1-azuloyl chlorides, e.g. (83)[152]. In the presence of aluminium chloride, azulene and phosgene give the ketone (82)[153]. The reaction of azulenes with cyanogen bromide give 1-cyanoazulenes[153,155], which are also accessible by dehydration of 1-azulenealdoximes with acetic anhydride[155] or methyl iodide[154].

AVII 6 Formylation of Azulenes

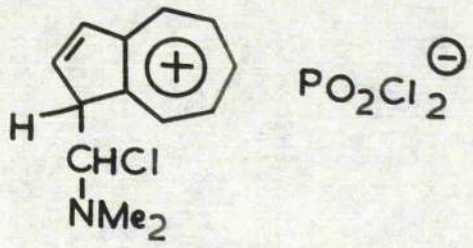
Passage of hydrogen chloride into a suspension of zinc cyanide in an ethereal solution of guaiazulene affords 3-formylguaiazulene (84). This is also obtained when 3-guaiazuleneglyoxylic acid is heated in aniline at 150°, and the resulting Schiff's base is hydrolysed by dilute hydrochloric acid[148].

The Vilsmeier reaction[156] is generally applicable to the preparation of 1-formylazulenes. A mixture of dimethyl formamide and phosphorus oxychloride is considered to react through the intermediate salt $(Me_2N\text{-}\overset{+}{C}H\text{-}Cl)\ (PO_2Cl_2)^-$. With azulene[72,71] this initially forms the unstable intermediate

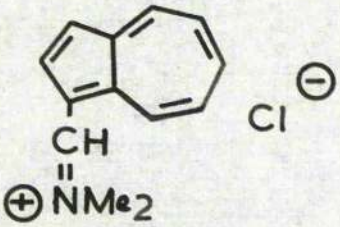
(85), which leads to the salt (86). This can be isolated, hydrolysis affording 1-formylazulene (87).



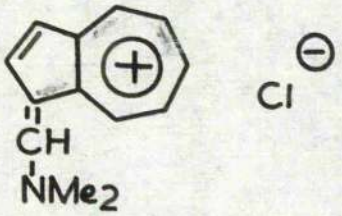
(84)



(85)

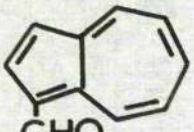


(86a)

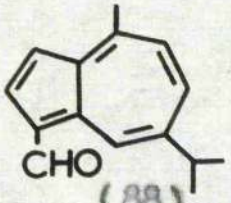


(86b)

Other methods of formylation in the 1(3)-positions involve the condensation of azulenes with ethyl orthoformate in the presence of strong acids (CV), and, in the isolated case of guaiazulene[157], oxidation of the 1-methyl group by selenium dioxide, to give (88).



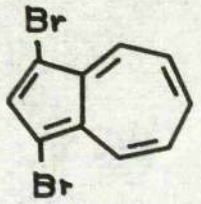
(87)



(88)

AVII 7 Halogenation of Azulenes

Several mono- and di-halogenoazulenes have been prepared by the reaction of azulenes with N-halosuccinimides[139]. Proof that the product of reaction between azulene and N-bromosuccinimide is 1,3-dibromoazulene (89) was obtained by degradation of 1,3-diacetylazulene (74) with sodium hypobromite, which yielded the same product[158].

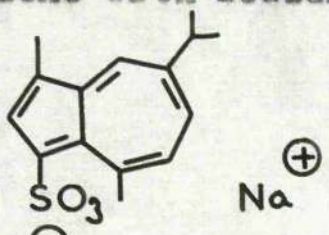


(89)

1-Bromo-4,6,8-trimethylazulene is reported to form a Grignard reagent[153].

AVII 8 Sulphonation of Azulenes

Sulphonation is readily effected by sulphuric acid in acetic acid, oleum, or sulphur trioxide in dioxane[159,160]. Proof that the 3-position of guaiazulene is attacked was obtained by degradation of the sodium salt (90) of the sulphonation product, to 3-chloroguaiazulene, by phosphorus oxychloride[161]. This is independently accessible by treatment of 3-acetylguaiazulene with sodium hypochlorite, and by



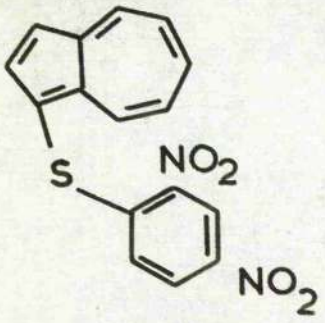
(90)

direct substitution of guaiazulene using N-chlorosuccinimide.

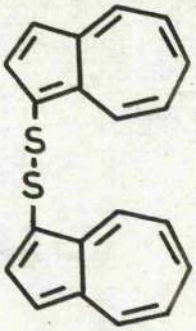
AVII 9 Reaction of Azulenes with Miscellaneous Electrophilic Reagents.

2,4-Dinitrobenzenesulphonyl chloride reacts with azulene to give (91), which with methanolic alkali gives di-1-azulenyldisulphide (92). Thiocyanogen reacts to give either of the substitution products (93) or (94), depending on the temperature. Attempts to prepare azulene thiols from these

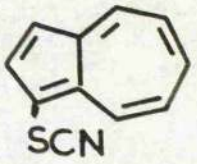
compounds were unsuccessful[162].



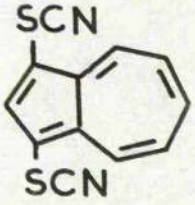
(91)



(92)



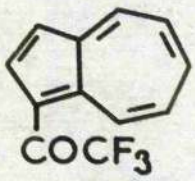
(93)



(94)

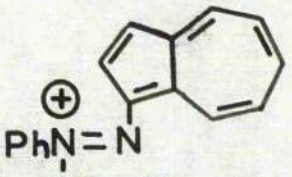
Dichloromercuriazulenes are easily obtained in high yield. Azulenes are about as reactive as pyrrole in this sense[27].

Reaction of azulene with trifluoracetic anhydride in carbon tetrachloride gives 1-trifluoracetylazulene (95). The position of attack followed conclusively from the



(95)

(96)

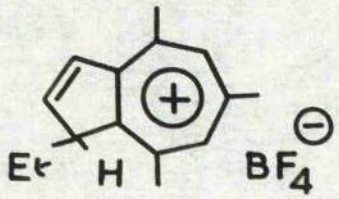


(97)

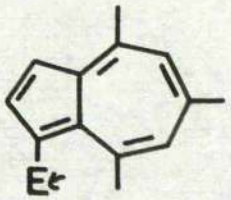
degradation of (95) with alcoholic sodium hydroxide to the known azulene-1-carboxylic acid. 1-Chloroazulene gives the expected product (96), but 1-nitroazulene and 1-phenylazoazulene do not react. The latter appears to undergo a reaction analogous to reversible protonation, to form (97)[163].

Trimethyloxonium fluoroborate was reported not to react with azulenes[27]. Subsequently, however, triethyloxonium fluoroborate reacted with 4,6,8-trimethylazulene to yield the fairly stable salt (98), which on hydrolysis gives 1-ethyl-

-4,6,8-trimethylazulene (99)[164].

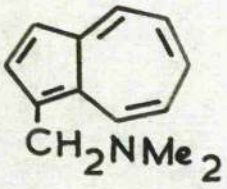


(98)

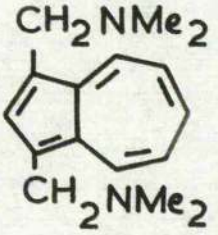


(99)

Dimethylaminomethylation of azulene may be achieved by treatment of azulene with bis(dimethylamino)methane, paraformaldehyde, and acetic acid in benzene[165]. A recent improvement on this is to use dimethylaminomethanol and perchloric acid, followed by potassium carbonate. Both the mono-(100) and di-substituted (101) compounds are available in this way[166].



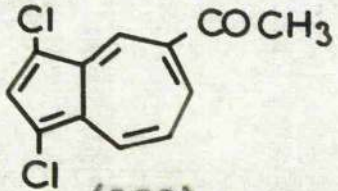
(100)



(101)

With tetracyanoethylene, azulenes give π complexes and/or 1(3)-tricyanovinylazulenes. Formation of the complex is favoured when the azulene is alkylated in the 1- and 3-, or 4- and 8- positions[167].

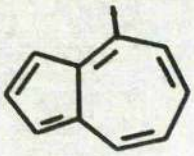
1,3-Dichloroazulene, where both preferred sites for electrophilic attack are occupied, has been acetylated in the 5- position, giving (102)[168].



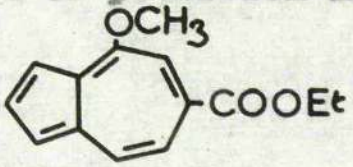
(102)

AVIII Azulenes:- Nucleophilic Substitution

From theoretical considerations, position 4(8) of azulene is the preferred site for nucleophilic attack[132,133,134,169]. The experimental data so far available confirms these predictions. Organometallic compounds, such as methyl lithium, attack azulene to give, in this case, after hydrolysis and dehydrogenation with chloranil, 4-methylazulene (103). Repetition of this process gives the 4,8-disubstituted azulene[75]. Methoxide ion in the form of potassium methoxide



(103)

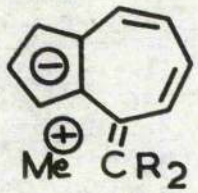


(104)

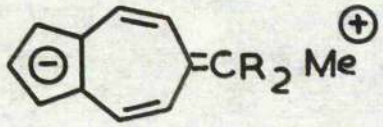
destroys the azulene nucleus[170]. However, when ethyl-4--methoxyazulene-6-carboxylate (104) is treated with boiling ethanolic or aqueous potassium hydroxide, the methoxy group is replaced by an ethoxy or hydroxy group respectively[170].

Sodamide in liquid ammonia with azulene gives an unstable red basic product, whose spectrum is consistent with it being 4- or 6-aminoazulene. In acid solution this compound is colourless, which shows that the azulene nucleus is protonated, in preference to the nitrogen atom[170].

Compounds of the type (105) and (106) have been reported (as yellow crystals) from the reaction of azulene with metal alkyls and sodium methylanilide, and 4,8-disubstituted azulenes are attacked by lithium alkyls in the 6- position[171].



(105)



(106)

AIX Azulenes:- Substitution by Radicals

The factors which determine the course of free radical reactions are not so well defined as those for electrophilic and nucleophilic reagents. The most relevant theoretical quantity appears to be the atom localisation energy[172]. Essentially this indicates the potential energy barrier against assumption of the required transition state for reaction to proceed. Later[173] the idea of free-valence was introduced by Coulson. The free valence number is a meaasure of the amount of additional bonding in which an atom can take par t, and hence provides an index for homolytic reactivity. Calculations of these two quantities are shown in Table 1.

Position on Azulene Nucleus	1(3)	2	4(8)	5(7)	6	9(10)
Atom localisation energy ( )[132,133]	2.26	2.36	2.24	2.34	2.36	-
Free valence*	.480	.420	.482	.429	.454	.149

Table 1

* Calculated from Huckel's L.C.A.O. - M.O. approximation[63].

Thus both approaches lead to the prediction that position 4- will be the preferred site for free radical attack, although the difference between the 1- and 4- positions is slight.

Experimental evidence available at present shows that the 1- and/or 2- position is attacked. Phenyl radicals give 1-phenylazulene in low yield[74,174]. Benzoyloxy radicals yield 1-benzoyloxyazulene[174], and benzyl radicals give a mixture of 1- and 2-benzyl azulene, in comparable amounts, with a small quantity of an unknown pentabenzylazulene[54].

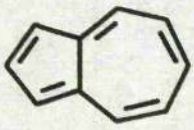
Since the calculated preferences are small, it is likely that steric factors exert a dominating influence on the course of reaction.

P A R T B.

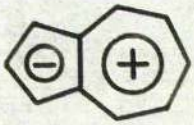
BI Condensation of Azulenes with Aldehydes in the Presence of Strong Acids

BI1 Introduction to Condensations with Carbocyclic and Heterocyclic Aromatic Aldehydes

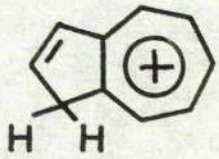
The polarisability of azulene, whose polarisation is symbolised by (1a) ⟷ (1b), is manifested by the ease of formation of the azulenium ion (2). It should be possible to replace $=CH_2$ by $=C=C.R_1R_2$, with retention, and even enhancement of the stability, of the tropylium structure.



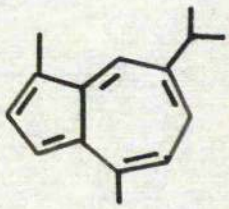
(1a)



(1b)

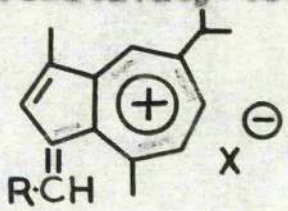


(2)

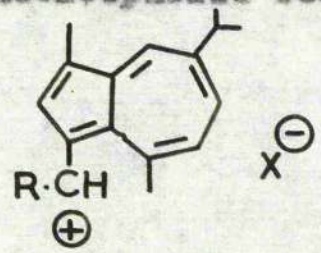


(3')

Previously[126,127,175] it was shown that guaiazulene (3') condenses with many aromatic aldehydes in ether containing anhydrous hydrogen chloride to give arylmethyleneguaiazulenium chlorides ((3) X = Cl). The products (3) are salt like substances, soluble in polar solvents such as acetone or acetic acid, and insoluble in ether and hydrocarbons. They show marked reactivity towards nucleophilic reagents. The



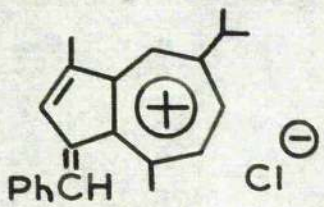
(3a)



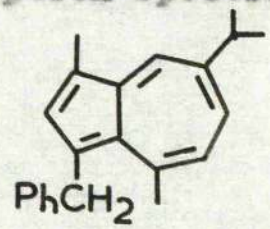
(3b)

structure of the 3-benzylideneguaiazulenium chlorides, e.g. (4), was confirmed by reduction with lithium aluminium hydride to

substituted 3-benzylguaiazulenes, e.g. (5), which were identified by their visible absorption spectra.



(4)



(5)

However, the majority of these chlorides tend to decompose, even at room temperature. Satisfactory analyses could not be obtained, but treatment of the freshly prepared chlorides in acetic acid with saturated aqueous picric acid afforded the corresponding picrates, which were stable for considerably longer periods, and gave satisfactory analyses, but neither these nor the chlorides could be recrystallised from hot solvents without decomposition. Also, molecular extinction coefficients of absorption for the visible and ultra-violet regions could not be measured.

The products of condensation of guaiazulene with heterocyclic and aliphatic aldehydes could not be isolated by this method, although in many cases reaction was shown to have taken place by the consumption of guaiazulene, the appearance of the expected colours, and the behaviour of solutions containing the reaction products.

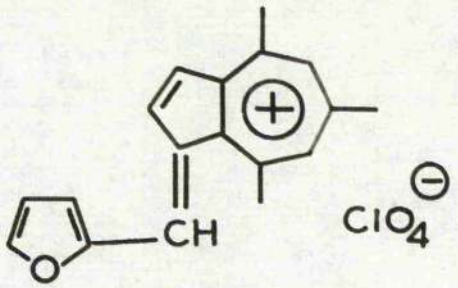
The work described in section BI is concerned with the improvement of the older method of preparation of salts containing substituted 1(3)-benzylideneazulenium cations,

and with the subsequent application of the improved method in a study of the condensations of azulenes with heterocyclic aromatic, and aliphatic aldehydes.

BI2 Condensations with Carbocyclic and Heterocyclic Aromatic Aldehydes in the Presence of Perchloric Acid

A possible contributing factor to the instability of the 1(3)-arylideneguaiazulenium chlorides is the relatively high nucleophilic character of the chloride ion. A suitable alternative appeared to be the perchlorate ion which could be supplied generally in the form of perchloric acid. A modified procedure was developed from this viewpoint, in which equimolar proportions of a homocyclic or heterocyclic aromatic aldehyde and guaiazulene were allowed to interact with an excess of perchloric acid in acetic acid, tetrahydrofuran, or acetonitrile. Reaction usually occurred at room temperature, although a short period of boiling was sometimes expedient. The perchlorates were readily isolated in high yield as coloured, beautifully crystalline, salts. They generally withstood repeated recrystallisation from acetic acid or acetonitrile without decomposition. Azulene (1) itself condensed in a similar fashion to give less stable products, which decomposed more or less rapidly on attempted recrystallisation from hot solvents. One derivative of 4,6,8-trimethylazulene was prepared, viz., 1-2'-furylidene--4,6,8-trimethylazulenium perchlorate(6) (CI25). It possessed the same order of stability as the products from

guaiazulene.



(6)

It is thus apparent that, other factors being the same, alkylation of the azulene nucleus makes an important contribution to the stability of the 1(3)-arylideneazulenium cation. This fact may be rationally interpreted by assuming that the inductive/hyperconjugative electron release of the alkyl groups lowers the electrophilic character of the cation.

BI3 Visible Spectra of 1(3)-Arylmethyleneazulenium Perchlorates

The series of 3-benzylideneguaiazulenium perchlorates which were prepared (CI) enable comparisons to be made of the effect of substituents in the benzene ring on the spectrum of the cation. The visible absorption maxima for this series are shown in Table 1. In most cases the visible spectrum consists of a single broad band devoid of fine structure, sometimes with a second maximum in the near visible region (360 - 380 m.μ.). Table 2 shows the visible absorption maxima for the corresponding products from azulene which could be isolated. None of them were sufficiently stable to allow determination of the extinction coefficients. The differences between the absorption maxima and those of the corresponding guaiazulene derivatives (Table 1) are also

R	λ Max. (m.μ.)	Log ε	Ref.	R	λ Max. (m.μ.)	Log ε	Ref.
Ph	456	4.09	CI 1	p-Cl.C_6H_4	454	4.00	CI 11
1-naphthyl	503	4.30	CI 3	m-O_2N.C_6H_4	438	3.97	CI 12
3-pyrenyl	597	4.41	CI 2	p-O_2N.C_6H_4	435(sh.)	3.74	CI 13
o-HO.C_6H_4	499	4.28	CI 4	2'-furyl	505	4.56	CI 14
m-HO.C_6H_4	475	4.18	CI 8	2'-thienyl	505	4.53	CI 15
p-HO.C_6H_4	523	4.51	CI 5	3'-indolyl	582	4.10	CI 16
p-MeO.C_6H_4	515	4.45	CI 6	2'-pyridyl	410	3.80	CI 17
2'4'-$(HO)_2$.C_6H_3	563	4.67	CI 9	4'-pyridyl	420(inf)	3.70	CI 18
3'4'-(-O-CH_2-O-)C_6H_3	531	4.43	CI 10	2'-quinolinyl	425	4.15	CI 19
p-Me_2N.C_6H_4	647	4.98	CI 7	4'-quinolinyl	435(sh.)	3.88	CI 20

Table 1 Visible absorption maxima (acetic acid) of 3-(R-methylene)guaiazulenium perchlorates.

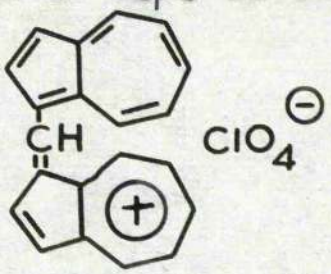
Notes:- (sh.) = shoulder, (inf.) = inflection.

R	λ Max. (m.μ.)	$\Delta\lambda$ Max., relative corresponding guaiazulene derivative (m.μ.)	Ref.
p-HO·C_6H_4	500	-23	CI21
p-Me_2N·C_6H_4	635	-12	CI22
2-furyl	496	-9	CI23
3-indolyl	560	-22	CI24

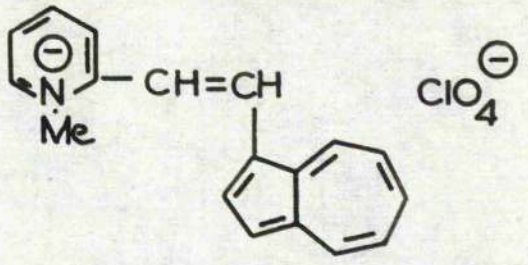
Table 2 Visible absorption maxima (acetonitrile) of 1-(R-methylene) azulenium perchlorates.

shown (Table2).

These displacements compare with a difference of 23 m.μ. observed between the absolute absorption maxima for azulene (Table 21) and guaiazulene[8]. It is interesting to compare this with other systems containing the azulenium structure. In the series of 1,1'-azulenylmethyleneazulenium perchlorates (see BIII), of which (7) is the parent, a bathochromic displacement of 26 m.μ. is observed when one azulene nucleus is



(7)

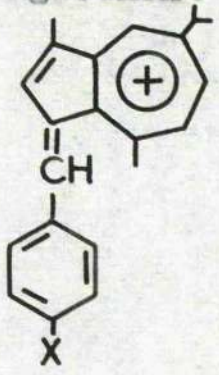


(8)

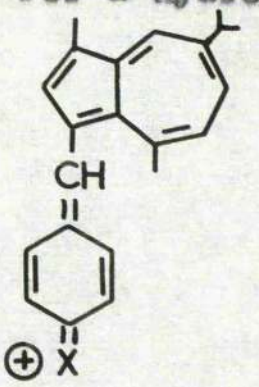
replaced by guaiazulene. Among the dimethine cyanine salts produced by condensation of a 1-formylazulene with a heterocyclic quarternary ammonium salt, e.g. (8) (see CIV), replacement of the azulene by the guaiazulene nucleus produces

a shift of from +36 to +51 mμ., depending on the heterocyclic nucleus.

Table 3 is constructed from the data of Table 1, and shows the effect of substitution in the phenyl group of the 3-benzylideneguaiazulenium perchlorate on its visible absorption spectrum. Either annelation on the introduction of electron releasing substituents into the benzene ring produces a bathochromic shift in λmax. and increases the intensity of absorption (Plate I). This is doubtless explained by the extension of the molecular orbital of the 3-benzylideneguaiazulenium cation. Here, for instance, an electron releasing group is substituted in the p- position ((9a); X is electron releasing), the contribution of resonance forms of type (9b) is enhanced by the assumption of an electron pair from the substituent. The variations are in good agreement with theory. For a hydroxyl group



(9a)



(9b)

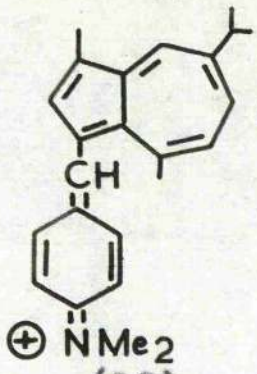
the effectiveness of electron release at different positions follows the order p > o > m, and the shifts in λmax. are almost additive. For example, the shifts for o-hydroxyl and

Modified Phenyl Group of 3-Benzylideneguaiazulenium Perchlorate	$\Delta\lambda_{Max.}$ (mμ.)	Δ Log ε	Ref.
1-naphthyl	+47	+0.21	CI3
3-pyrenyl	+141	+0.32	CI2
o-hydroxyphenyl	+43	+0.19	CI4
m-hydroxyphenyl	+19	+0.09	CI8
p-hydroxyphenyl	+67	+0.42	CI5
p-methoxyphenyl	+59	+0.36	CI6
2,4-dihydroxyphenyl	+107	+0.58	CI9
3,4-(-O-CH_2-O-)phenyl	+75	+0.34	CI10
p-dimethylaminophenyl	+191	+0.89	CI7
p-chlorophenyl	-2	-0.09	CI11
m-nitrophenyl	-18	-0.12	CI12
p-nitrophenyl	-21	-0.35	CI13

Table 3 Effect on spectrum of 3-benzylideneguaiazulenium perchlorate of modification of the phenyl group.

p-hydroxyl are +43 and +67 mμ. respectively. The two in combination should therefore give a shift of +110 mμ.; the observed shift for 2,4-dihydroxyl derivative is +107 mμ.

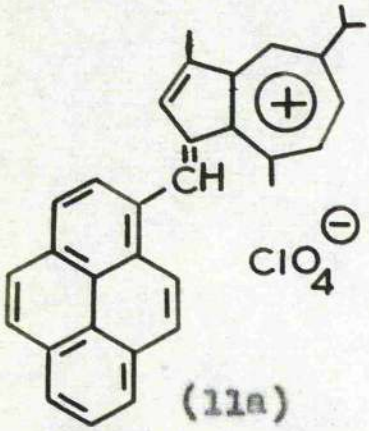
The p-dimethylamino group causes the greatest shift (+191 mμ.), with a nine-fold increase in the extinction coefficient (CI7). The difference between this compound and the p-methoxyl derivative reflects the greater availability of the free electron pair of the nitrogen atom compared to oxygen, and polar forms such as (10) must therefore make substantial contributions to the structure. The position



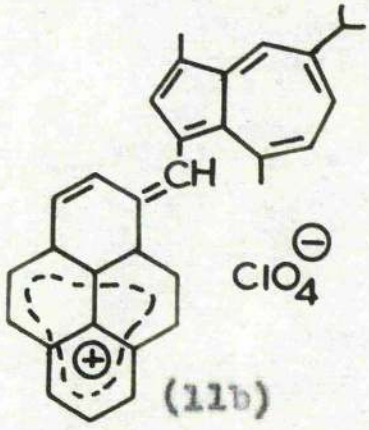
(10)

and intensity of the absorption emphasise the similarity of this structure with the series of 1,1'-azulenylmethylene-azulenium salts (BIII), where the positive charge resonates between two seven-membered rings.

The salt with the next greatest displacement is that derived from 3-formylpyrene (11a) (CI2). Here again a substantial contribution from alternative resonance forms, e.g. (11b), is to be expected, since considerable stability attends the delocalisation 12 π electrons over 13 carbon nuclei[121], and the cation in the limiting structure (11b) may



(11a)



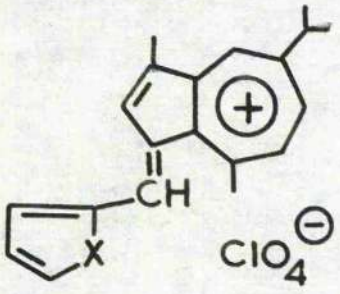
(11b)

be regarded as a substituted perinaphthenylium cation.

A p-chloro substituent (CI1) has hardly any effect on the spectrum, but an electron attracting substituent causes a hypsochromic displacement, and slightly reduces the

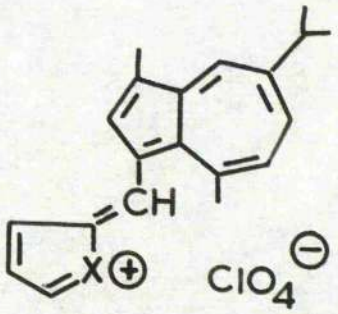
extinction coefficient. Thus the m-nitro group (CI12) causes a displacement of -18 m.μ., and the p-nitro derivative (CI13) has a shoulder at 435 m.μ. ($\Delta\lambda max.$ = -21 m.μ.). The visible maxima (at C. 450 m.μ.) of those salts with electron attracting substituents in the phenyl group are submerged, to a greater or lesser extent, in an absorption curve which rises to a maximum at about 370 m.μ. (see Plates I, III, and IV).

The condensation products from heterocyclic aromatic aldehydes fall into two groups. The spectral displacements relative to 3-benzylideneguaiazulenium perchlorate are shown in Table 4. The indole nucleus, and similarly furan and thiophen, behaves qualitatively in the same way as a phenyl group carrying an electron releasing substituent. The spectra of the derivatives from furan (12) and thiophen (13) closely resemble that of p-hydroxybenzylideneguaiazulenium perchlorate (see Plate II).



(12a)

(13a)



(12b) X = O

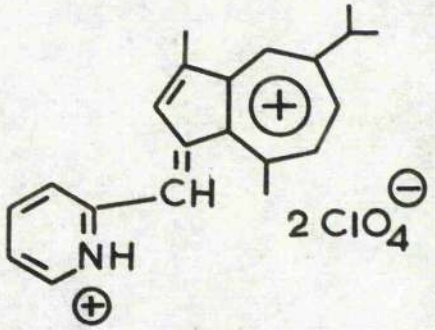
(13b) X = S

The products from 2-formylpyridine (14) and 4-formylpyridine and 2- and 4-formylquinoline are diperchlorates,

in which a proton has added to the ring nitrogen atom. This enhances the electron attracting effect of the heterocyclic nucleus, and their spectra resemble those of m- and p-nitrobenzylidineguaiazulenium perchlorates (see Plates III and IV), showing a hypsochromic displacement of λmax., and, except for the 2-quinoline derivative, a lowering of the absorption intensity.

R	$\Delta \lambda$max. (mμ.)	Δ Log ε	Ref.
2-furyl	+49	+0.47	CI14
2-thienyl	+49	+0.44	CI15
3-indolyl	+126	+0.01	CI16
2-pyridyl	-46	-0.29	CI17
4-pyridyl	-36	-0.39	CI18
2-quinolinyl	-31	+0.06	CI19
4-quinolinyl	-21	-0.21	CI20

Table 4 Effect on spectrum of 3-benzylideneguaiazulenium perchlorate when the phenyl group is replaced by a heterocyclic nucleus (R).



(14)

The condensation of azulenes with 1-formylazulenes in

the presence of strong acids logically forms an extension of this section, but is conveniently discussed in Section BIII, together with other methods of synthesising 1,1'-azulenylmethyleneazulenium salts.

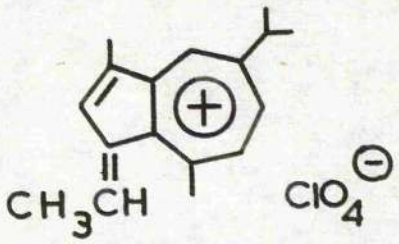
BI 4 Introduction to Condensations with Aliphatic Aldehydes

A much more complex reaction picture emerges from a study of the condensations of azulenes with aliphatic aldehydes in the presence of perchloric acid. In many cases the products do not correspond to a simple condensation of one molecule each of the azulene, the aldehyde, and perchloric acid, as in the condensations with aromatic aldehydes, although such a condensation may apparently take place as a primary reaction step. The primary product may then be susceptible to further reaction, as will be seen in the following sections. Also, in many of these reactions, alkylated azulenes behave differently from azulene, due to electron release by the alkyl groups which increases the electron availability at position 1-, and stabilises the 1-methyleneazulenium structure of the primary condensation product.

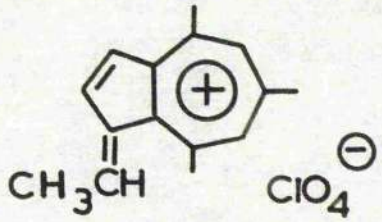
BI 5 Condensations with Simple Aliphatic and Unsaturated Aldehydes

Acetaldehyde was found to condense readily with guaiazulene, and 4,6,8-trimethylazulene, to give the stable yellow salts 3-ethylideneguaiazulenium perchlorate (15) and

1-ethylidene-4,6,8-trimethylazulenium perchlorate (16) respectively. (CI26, CI27) (For spectra see Plate V). These products are quite stable at room temperature, but decompose partly on attempted recrystallisation from acetic



(15)

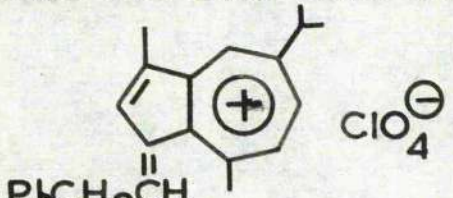


(16)

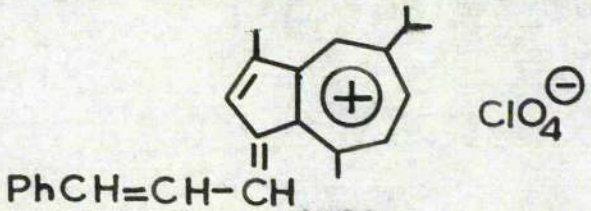
acid or acetonitrile. No useful product could be isolated from an identical condensation with azulene. The salts are very similar in appearance to the 1-hydroxy and 1-ethoxy-methyleneazulenium salts (see (BII3) and (BIII3)). They are readily reduced by lithium aluminium hydride (e.g. see (DIX)) to the corresponding 1-ethylazulene. The combined reactions thus provide a very convenient method of introducing a 1(3)-ethyl substituent into an azulene nucleus, where the 1(3)-ethylideneazulenium salt can be isolated. This is considerably simpler than the procedure involving triethyl-oxonium fluoroborate, which was used by Hafner to convert 4,6,8-trimethylazulene into 1-ethyl-4,6,8-trimethylazulene[164].

The effect of replacing the methyl hydrogen atoms of acetaldehyde was investigated. When these groups were electron releasing (e.g. using propionaldehyde, n-butyraldehyde, isobutyraldehyde, and ethoxyacetaldehyde), condensation with guaiazulene or 4,6,8-trimethylazulene invariably failed to

take place. Substituted acetaldehydes in which a methyl hydrogen atom is replaced by electron withdrawing substituents all condensed with azulenes. Phenylacetaldehyde with guaiazulene and perchloric acid gave 3-2'-phenylethylidene-guaiazulenium perchlorate (17), which, however, could not be purified. The corresponding product from 4,6,8-trimethyl-azulene was even less stable, and decomposition prevented



(17)



(18)

its isolation. Crotonaldehyde condensed very vigorously with guaiazulene, but no product could be isolated from the greenish-yellow solution. Cinnamaldehyde condensed with guaiazulene to give the red product (18). Although cinnamaldehyde is formally an $\alpha\beta$ unsaturated aliphatic aldehyde, it closely resembles benzaldehyde in its reaction with guaiazulene.

BI 6 Visible Spectra of the Products of Condensation with Acetaldehyde and Cinnamaldehyde

The visible absorption maximum of (18) shows a bathochromic displacement and increased intensity relative to 3-benzylideneguaiazulenium perchlorate ((3); R=Ph, X=ClO_4). This is as expected, since the additional vinyl group, in conjugation with the benzene ring, allows an extension of the molecular orbital of the cation. Spectral data for these

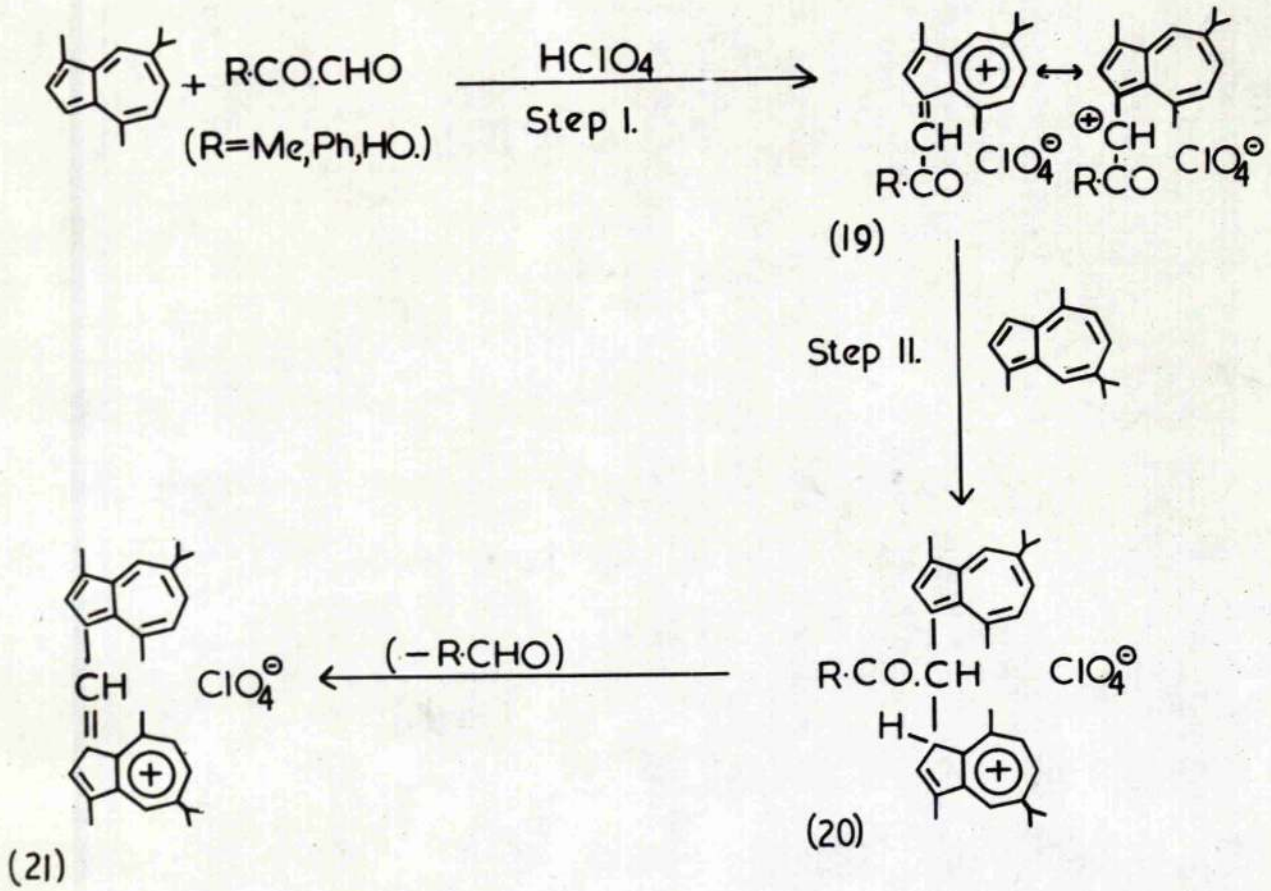


Fig.1. Reaction of guaiazulene with α-oxoaldehydes in the presence of perchloric acid.

products from aliphatic aldehydes are given in Table 5. (see Plates V and VI).

Aldehyde	Azulene	Product	λMax. (mμ.)	Log ε	Solvent	Ref.
Acet-aldehyde	guaiazulene	(15)	425(sh.) 370	3.45 3.75	Acetic acid	CI26
Acet-aldehyde	4,6,8-tri-methyl-azulene	(16)	405(b)	3.66	Aceto-nitrile	CI27
			440(sh.) 395	3.50 3.70	Acetic acid	
Cinnam-aldehyde	Guaiazulene	(18)	513	4.63	Acetic acid	CI28

Table 5 Visible absorption maxima of salts from the condensation of azulenes with acetaldehyde and cinnamaldehyde.

Notes: (a) Containing 2% (v/v) perchloric acid

(b) - Broad maximum.

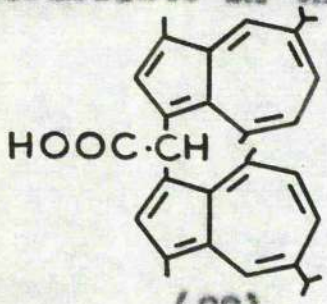
(sh.) Shoulder.

BI 7 Condensations with α-Oxoaldehydes

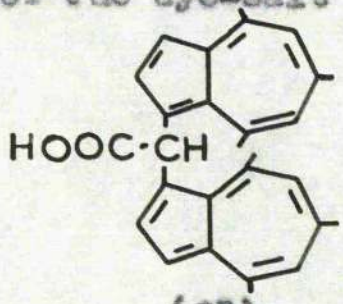
In this class of reactions the primary condensation product, an oxomethyleneazulenium perchlorate, is reactive, and may react further with the azulene at either the methine or carbonyl carbon atom. Pyruvic aldehyde, phenylgyoxal, and glyoxylic acid all condensed[176] with guaiazulene to yield the same product, 3-(guaiazulen-3-yl)methyleneguaiazulenium perchlorate (21) (Fig. 1). To interpret this, the reaction scheme outlined in Fig. 1 is suggested. In the primary step (I), the α-oxoaldehyde, R·CO.CHO, condenses normally to

form a 3-acylmethyleneguaiazulenium perchlorate (19). Unreacted guaiazulene subsequently attacks (19) at the electrophilic methine carbon atom (Step II) to yield the dye-salt (21). The resonance stability of structure (21) promotes the elimination of R•CHO from the intermediate (20).

In the absence of perchloric acid, glyoxylic acid behaves differently, reacting exothermally with guaiazulene in boiling acetonitrile to give di-(guaiazulen-3-yl)acetic acid (22) in high yield[176]. This product (22) is not an intermediate in the formation of the dye-salt (21) by



(22)



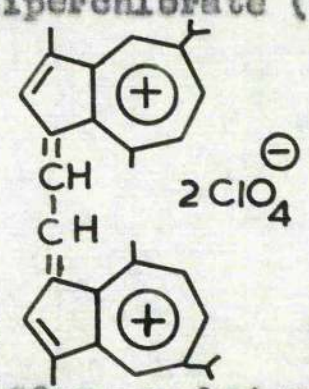
(23)

reaction in the presence of perchloric acid, since, when boiled with perchloric acid, (22) was not converted into the dye-salt (21)[176]. Azulene failed to react with glyoxylic acid alone, and in the presence of perchloric acid gave an unstable and unidentified acid.

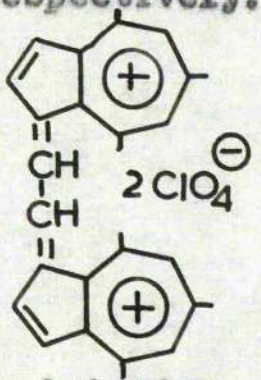
4,6,8-Trimethylazulene condensed with glyoxylic acid alone to give di(4,6,8-trimethylazulen-1-yl)acetic acid (23), together with a small amount of a second unstable acid whose structure was not established (CI32). The assignment of structure (23) to the main product is based on the similarity of its visible spectrum to that of (22) (see Plate VII).

The acids (22) and (23) both show on infra-red carbonyl stretching frequency (Nujol), at 1704 and 1701 cm.$^{-1}$ respectively. No product was obtained from 4,6,8-trimethylazulene and glyoxylic acid in the presence of perchloric acid.

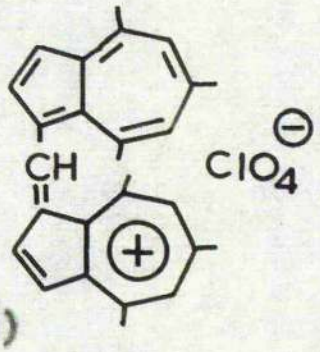
Glyoxal reacted with azulene[176] in a similar manner to the scheme outlined in Fig. 1, to give 1,1'-azulenylmethyleneazulenium perchlorate (7) in high yield. With guaiazulene[176] and 4,6,8-trimethylazulene (CI31) however, it behaved exceptionally among the α-oxoaldehydes in condensing at both aldehyde functions, to give ethanediylidenebis(3-guaiazulenium) diperchlorate (24), and ethanediylidenebis(1'-4,6,8-trimethylazulenium) diperchlorate (25) respectively.



(24)



(25)



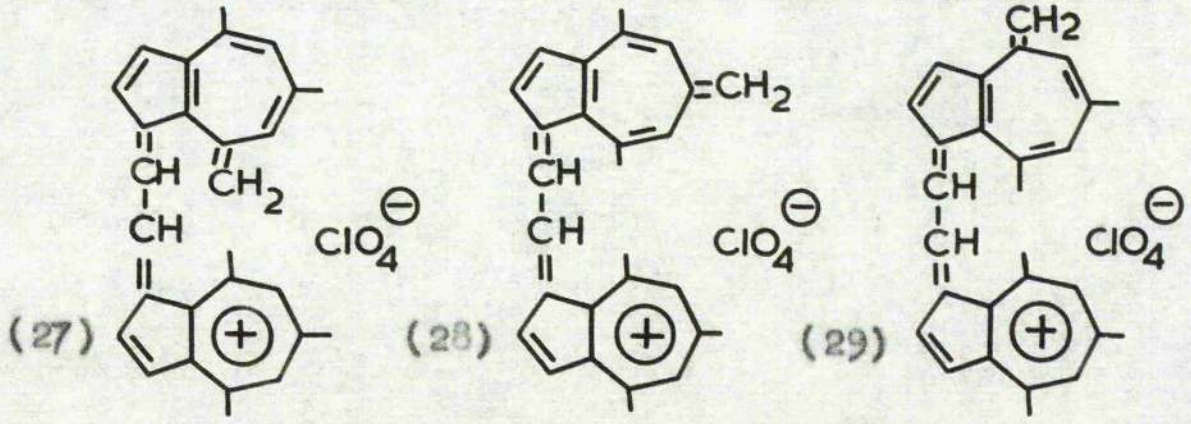
(26)

This difference between the behaviour of guaiazulene and 4,6,8-trimethylazulene on the one hand, and azulene on the other, is accounted for by the electron releasing effect of the alkyl groups, which lowers the electrophilic character of the methine carbon atom of the primary product to a level which is below that of the carbonyl carbon atom. As might be expected, the visible spectra of the two diperchlorates (24) and (25) differ markedly from those of the dye-salts

(21) and (26) (see Plate VIII), for although, formally, there is complete conjugation throughout the system, the effect of the two like charges within the molecule will be to tend to cause the structure to more resemble two 1(3)-methylene-azulenium cations linked by a single bond.

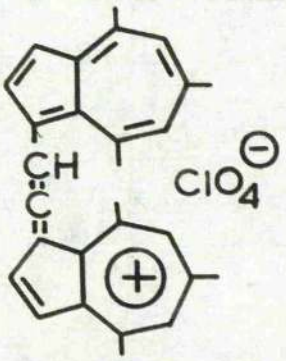
An interesting property of the product from 4,6,8-trimethylazulene, glyoxal, and perchloric acid (25), is its readiness to lose a molecule of perchloric acid to give a blue monoperchlorate of unknown structure. This has quite distinct properties. The diperchlorate (25) is only stable in the presence of an excess of perchloric acid, and when recrystallised from acetonitrile alone, yields the monoperchlorate. The monoperchlorate is much less soluble, and in its solubility, appearance (dark green needles), and visible spectrum (see Plate VIII), it bears a much closer resemblance to the 1,1'-azulenylmethyleneazulenium salts.

The most likely site for the loss of a proton from (25), consistent with the known properties of azulene, would be the 4-,6-, or 8- methyl groups. One of the structures (27), (28) or (29) would result, each of which would be stabilised



(27) (28) (29)

by resonance among several canonical structures. An alternative structure (30) could be derived by loss of a proton from one of the methine carbon atoms. It is uncertain



(30)

what the effect of an allene group in such a situation would be, but the evidence seems to exclude this possibility. It might be expected that the spectrum of (30) would resemble that of a 1-alkyl-4,6,8-trimethylazulene, assuming that there would be little interaction between the 4,6,8-trimethylazulene nucleus, and the 4,6,8-trimethylazulenium ion. However, the extinction coefficient ($\log \varepsilon = 4.71$) is much higher than would be expected for a molecule with an electronically isolated azulene nucleus, and suggests that delocalisation of the charge can take place over the whole molecule.

Further evidence against a structure of type (30) derives from recent work on the blue compound formed from 1,1-di(p-methoxyphenyl)ethylene and carboxylic acids[177]. The carbonium ion $(Ar_2C{=}CH{-}CH{-}CH{=}CAr_2)^+$ (Ar=p-methoxyphenyl) was isolated as a solid perchlorate, and this was proved to be derived from the structure $Ar_2C{=}C{=}CH{-}CH{=}CAr_2$ by the addition of acid. The point of note is that the latter is a colourless compound, whereas the protonated product has an

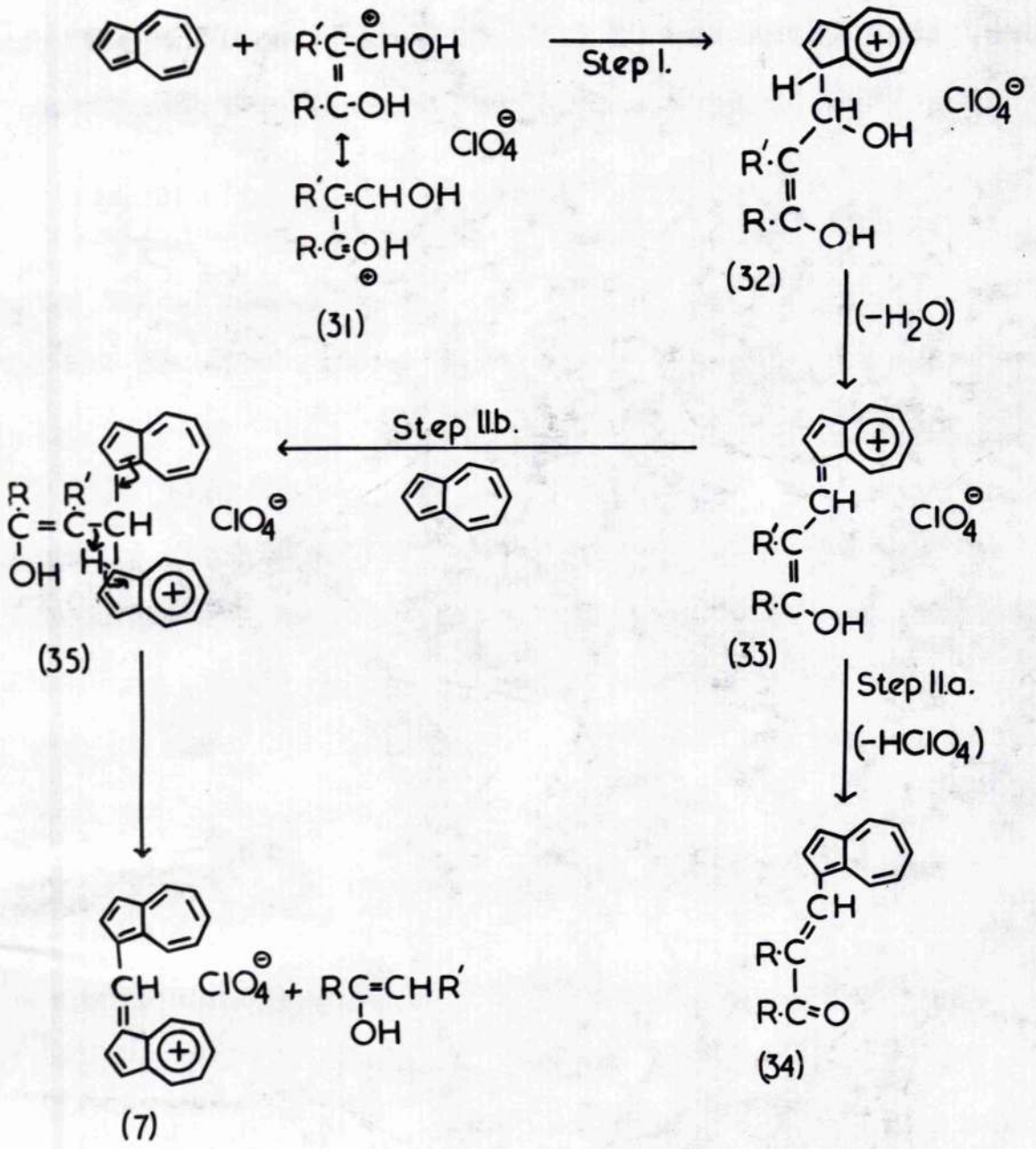


Fig. 2. Reaction of azulene with β-oxoaldehydes in the presence of perchloric acid.

intense absorption at 665 mμ. It hardly seems likely therefore, that formation of (30) from (25) would result in greatly increased intensity of absorption in the long wave region.

It was subsequently found[178] that the product from guaiazulene (24) behaves similarly, although loss of a molecule of perchloric acid does not take place quite so readily.

BI 8 Condensation with β-Oxoaldehydes

The products from the condensation of azulenes with β-oxoaldehydes were either 2-(azulen-1-yl)methylene ketones, or symmetrical 1,1'-azulenylmethyleneazulenium perchlorates, and with a suitable choice of reaction conditions, products of the former type could usually be isolated. The highly alkylated azulenes guaiazulene, and 4,6,8-trimethylazulene, however, never yielded more than a trace of the symmetrical dye-salts.

The reaction sequence suggested to account for these observations is outlined in Fig. 2., for the reaction between azulene and a 2-hydroxymethylene ketone, R.CO R.'C=CHOH. The ketone may be activated by protonation at either oxygen atom (see Fig. 3). Electrophilic attack of the azulene molecule by one of the activated forms of the ketone, e.g. (31), (Fig. 2. Step I), leads to (32), and, after subsequent elimination of water, to the primary condensation product (33), which is the perchlorate of the 2-(azulen-1-yl)methylene

ketone (34). This (33) corresponds to the product obtained from the condensation of an aromatic aldehyde with azulene, and may be hydrolysed to the ketone (34) (Fig. 2., Step IIa).

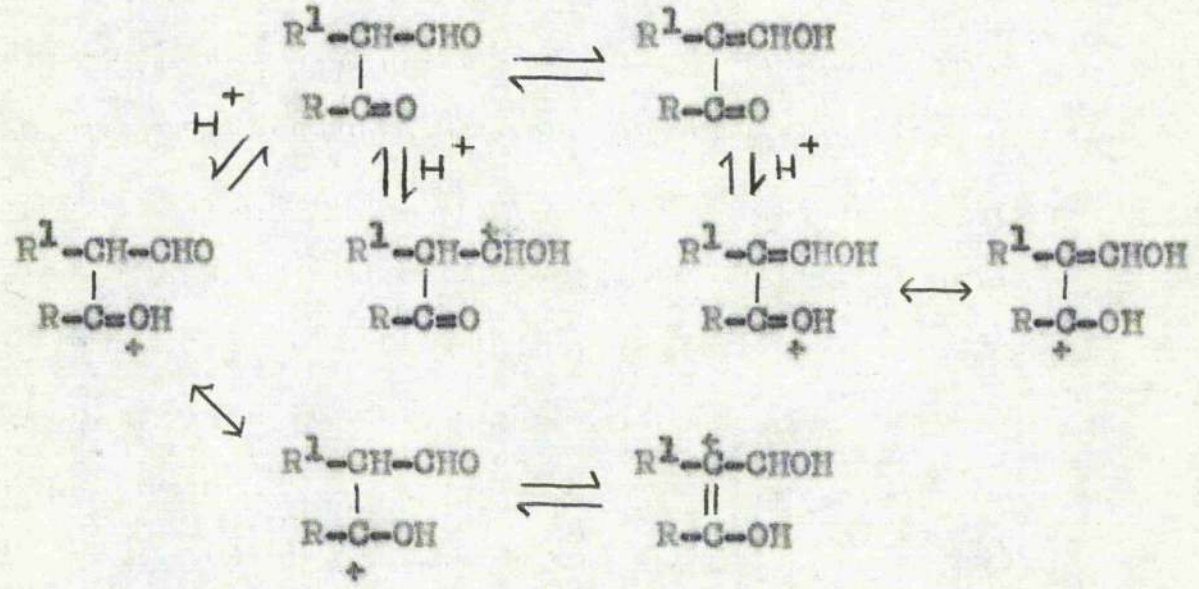
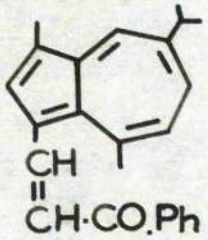


Fig.3 Activation of a β-Oxoaldehyde by Acid

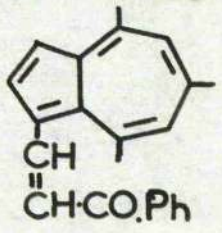
Further reaction at this stage with an excess of azulene (Fig. 2., Step IIb), via the intermediate (35), leads to the symmetrical dye-salt (7) and the ketone $R{\cdot}CO.CH_2R'$. The deactivating effect of alkyl substituents on the electrophilic methine carbon atom of the primary product determines the course of the secondary reaction, and the nature of the reaction products. Thus in condensations with azulene, the dye-salt (7) is much more easily obtained than the corresponding ones, (21) and (26), from condensations with guaiazulene and 4,6,8-trimethylazulene. Evidence for the reaction mechanism depicted (Fig. 2) comes from the isolation

of the ketone $R{\cdot}CO.CH_2R'$ from the condensation of azulene with 2-hydroxymethylenecyclohexanone, (CI39) and with hydroxymethyleneacetophenone (CI36). Further support comes from the isolation[176] of the dye-salt (7) from a boiling solution of azulene, 2-(azulen-1-yl)methylenecyclohexanone (38), and perchloric acid in acetic acid.

Hydroxymethyleneacetophenone condensed with guaiazulene and 4,6,8-trimethylazulene in boiling acetic acid with perchloric acid, to give the ketones (36) and (37), corresponding to the ketone (34) in Fig. 2. The ketone (37) is the only member of the series of 2-(azulen-1-yl)methylene



(36)



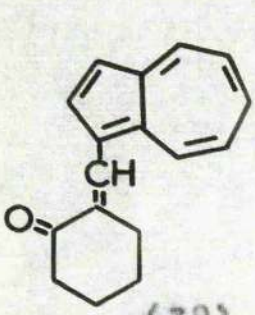
(37)

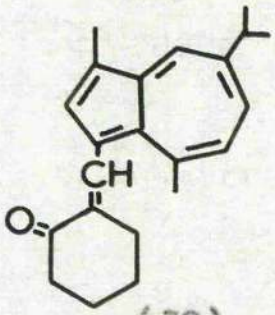
ketones which had previously been described. It was prepared[71] by condensation of 1-formyl-4,6,8-trimethylazulene with acetophenone. The physical data for this product (CI38) agree well with the reported values.

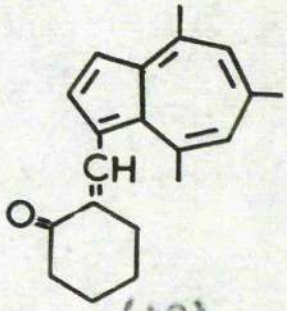
In contrast, azulene with hydroxymethyleneacetophenone gave 1,1'-azulenylmethyleneazulenium perchlorate (7) and a quantity of acetophenone, which was isolated from the reaction mixture as its 2,4-dinitrophenylhydrazone. 2-(Azulen-1-yl)methyleneacetophenone was not isolated (CI36).

2-Hydroxymethylenecyclohexanone behaved similarly, and

the three ketones (38) (39) and (40) were isolated in good yield, (CI39, CI40, and CI41). A trace of the dye-salts


(38)


(39)

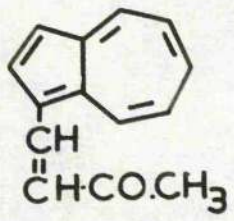

(40)

(21) and (26) were produced in the reactions with guaiazulene and 4,6,8-trimethylazulene respectively. With azulene, if reaction was carried out under the usual conditions (boiling acetic acid), the dye-salt (7) was the sole azulenic product, accompanied by cyclohexanone which was isolated as its 2,4-dinitrophenylhydrazone. However, when the condensation with azulene was carried out at room temperature in methanol, the main product was the ketone (38), only a trace of the dye-salt (7) being formed (CI39).

The ketones (41), (42), and (43) were isolated from the condensations of hydroxymethyleneacetone with azulene, guaiazulene, and 4,6,8-trimethylazulene respectively. (CI33, CI34, and CI35). The yield was very low in all cases, due presumably to rapid decomposition of free hydroxymethylene-acetone, which is known to trimerise readily[179]. Unreacted hydrocarbon was recovered in high yield in each case.

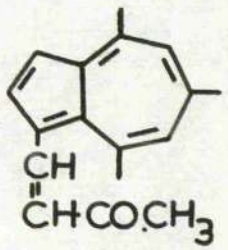
It might be argued that the structures assigned to these neutral products of condensation of azulenes with β-oxoaldehydes

are ambiguous, for it is conceivable that the primary condensation could occur at the keto- rather than the aldehyde function. In this case, the product of condensation of azulene with 2-hydroxymethylenecyclohexanone, for example, would have structure (44). It is doubtful whether infra-



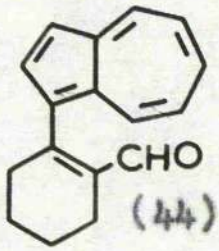
(41)

(42)



(43)

red data could distinguish between the two possibilities. However, the two facts that, (i), the ketone, (38) or (44),



(44)

when boiled with azulene and perchloric acid yields 1,1'-azulenylmethyleneazulenium perchlorate (7), and, (ii) cyclohexanone was isolated from the original reaction mixture of the experiment yielding the dye-salt (7) (CI39), conclusively demonstrate the correctness of structure (38). Similarly, acetophenone was isolated from the corresponding reaction between hydroxymethyleneacetophenone and azulene (CI36). This, the independent evidence for the structure (37)[71], the circumstantial evidence that no condensations of azulenes with a keto- carbonyl group alone have been found to occur

in the presence of perchloric acid, and the similarity in properties of the whole series of products, allows confidence in their formulation as 2-(azulen-1-yl)methylene ketones.

BI 9 Properties, and Visible, and I.R. Spectra of 2-(Azulen-1-yl)methylene Ketones

All the ketones prepared were yellow-green in solution, those from 4,6,8-trimethylazulene having a reddish tinge in transmitted light. These latter all crystallised, as brown needles. Those derived from azulene were yellow-green oils. Those from guaiazulene varied; most were oils, but some could be crystallised with difficulty. The visible spectra consisted in all cases of two broad absorption bands. (See Table 6, and Plates IX and X).

The carbonyl function reacts readily with 2,4-dinitrophenylhydrazine, and with perchloric acid the ketones revert to the perchlorates (e.g. CI37), having structures analogous to (33) (Fig. 2).

The infra-red carbonyl stretching frequencies for this series fall into two classes, depending on the nature of the second group attached to the carbonyl function (Table 7). When this is a saturated hydrocarbon residue as in (39) and (40), the frequencies are "normal", and the lowering of frequencies noticed in the 1-acylazulene series (BII 2) does not occur. On the other hand, where the other group is an aromatic ring, as in (36) and (37), $\nu_{C=O}$ remains close to that

Ketone	Solvent	λ max. (mμ.)	Log ε	Ref.
Guaiazulen-3-ylmethylene-acetophenone (36)	B	602 441 401	2.40 3.94 4.09	CI37
4,6,8-Trimethylazulen-1-ylmethyleneacetophenone (37)	B	563 424	2.92 4.46	CI38
Guaiazulen-3-ylmethylene-acetone (42)	A	604(b) 426(b)	(a)	CI34
4,6,8-trimethylazulen-1-ylmethyleneacetone (43)	B	560(b) 405(b)	2.88 4.34	CI35
Azulen-1-ylmethylene-acetone (41)	A	603(b) 436	(a)	CI33
2-(Guaiazulen-3-yl)-methylenecyclohexanone (39)	A	620(b) 427(b)	2.73 4.30	CI40
2-(4,6,8-Trimethylazulen-1-yl)methylenecyclohexanone (40)	A	526(b) 408(b)	2.84 4.24	CI41
2-(Azulen-1-yl)methylene-cyclohexanone (38)	A	612(b) 410(b)	(a)	CI39

Table 6 Visible absorption maxima of 2-(azulen-1-yl)methylene ketones.

Notes: (a) undetermined

(b) broad maximum

A Benzene

B Cyclohexane.

Ketone	Frequency (Cm^{-1}) Nujol	CCl4	Ref.
Guaiazulen-3-methyleneacetophenone (36)		1650	CI37
4,6,8-trimethylazulen-1-ylmethyleneacetophenone (37)	1634		CI38
2-(guaiazulen-3-yl)methylenecyclohexanone (39)	1664	1667	CI40
2-(4,6,8-trimethylazulen-1-yl)-methylenecyclohexanone (40)	1667	-	CI41
Guaiazulen-3-ylacetone (42)		1672 1656(a) 1631	CI34
Azulen-1-ylacetone (41)		1678 1672(a) 1653	CI33
3-Acetylguaiazulene	1642	1652	176
3-Benzoylguaiazulene	1637		148
3-Guaiazuloylguaiazulene	1594	1616	148
1-Acetylnaphthalene		1685	180
Benzylideneacetone		1666	181
Benzylideneacetophenone	1659		182

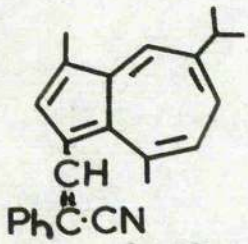
Table 7 Infra-Red carbonyl stretching frequencies of 2-(azulen-1-yl)methylene ketones and some related compounds.

Note: (a) Principal peak of a triplet.

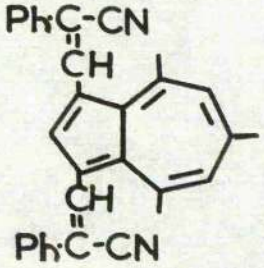
of the polarised 3-benzoylguaiazulene. The $\nu_{C:O}$ data for the substituted acetones (41) and (42) cannot be directly compared, since they show fine structure. The frequencies of the C:O absorption maxima for this series and some other related compounds are recorded in Table 7.

BI 10 Condensations with Hydroxymethylenephenylacetonitrile

Reactions in this series are very similar to those of the β-oxoaldehydes discussed in the foregoing section. Neutral products alone were obtained. Guaiazulene gave 3-(2-cyano-2-phenylvinyl)guaiazulene (45) (CI42) as a green oil, and 4,6,8-trimethylazulene reacted at both 1- and 3-positions to give 1,3-di(2-cyano-2-phenylvinyl)-4,6,8-trimethylazulene (46) (CI43) as a stable, high melting, crystalline



(45)

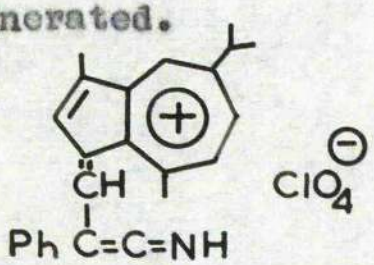


(46)

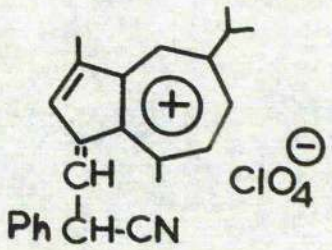
solid. Azulene[176] reacted similarly to give the corresponding disubstituted compound. Although the presence of perchloric acid is necessary to effect condensation of hydroxymethylenephenylacetonitrile with azulene, and 4,6,8-trimethylazulene, it is not required for the condensation with guaiazulene. The product (45) may also be obtained by merely boiling a solution of guaiazulene and hydroxymethylenephenylacetonitrile

in acetic acid.

In contrast to the behaviour of the ketone (36), the nitrile (45) does not form a stable perchlorate. When perchloric acid is added to a solution of (45) in acetic acid, the yellow-green colour changes to very pale yellow, presumably with concomitant formation of the salt (47) and/or (48), but on the addition of dry ether, the original colour is regenerated.



(47)



(48)

These condensations appear to involve an electrophilic attack by the methine carbon atom of hydroxymethylenephenylacetonitrile, or its N-protonated form in the case of azulene and 4,6,8-trimethylazulene, with subsequent elimination of a molecule of water, followed by a proton. The reaction thus appears to be entirely analogous to those of Steps I and IIa, Fig. 2.

BI 11 Visible and I.R. Spectra of 1(3)-, and 1,3-di(2-cyano-2-phenylvinyl)azulenes

The visible spectra (see Plate XI) closely resemble those of the 2-(azulen-1-yl)methylene ketones. The absorption maxima are shown in Table 8.

The C≡N has a lower than "normal" frequency when the

cyano group is attached to an azulene nucleus. This is exemplified by a comparison of the C≡N frequencies for 1-cyanonaphthalene and 3-cyanoguaiazulene (Table 9). The nitriles (45) and (46) also show a lowering of frequency, but to a smaller extent.

Nitrile	Solvent	λ max. (mμ.)	Log ε	Ref.
3-(2-cyano-2-phenylvinyl)-guaiazulene (45)	A	615 448	2.87 4.47	CI42
1,3-Di(2-cyano-2-phenyl-vinyl)azulene	B	605 428	2.96 4.58	176
1,3-Di(2-cyano-2-phenyl-vinyl)-4,6,8-trimethyl-azulene (46)	A	560 426	3.05 4.40	CI43

Table 8 Absorption maxima of 1(3)- and 1,3-di(2-cyano--2-phenylvinyl)azulenes.

Note: A Benzene

B Acetonitrile.

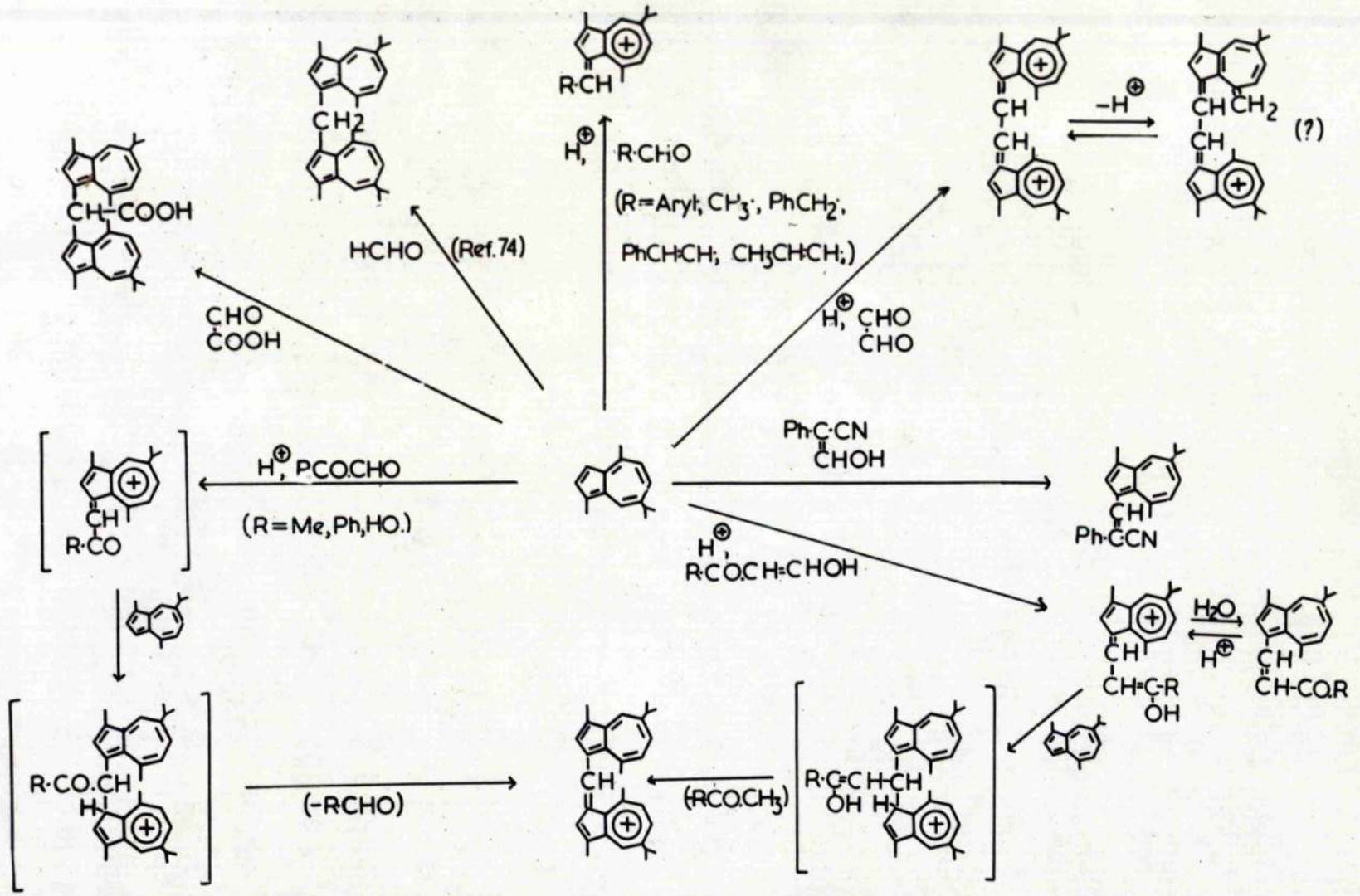


Fig.4. Reactions of guaiazulene with aldehydes: summary. No examples of the structures in parentheses have been isolated.

Nitrile	C≡N Stretching Frequencies (Cm^{-1}) Nujol	CCl4	Ref.
3-(2-Cyano-2-phenylvinyl)-guaiazulene (45)	2188	2203	CI48
1,3-Di(2-cyano-2-phenyl-vinyl)azulene	2198	-	176
1,3-Di(2-cyano-2-phenyl-vinyl)-4,6,8-trimethyl-azulene (46)	(2210? (2191	(2284? (2209	CI43
3-Cyanoguaiazulene	2183	2201	148
1-Cyanonaphthalene	2212	2222	176

Table 9 ν C≡N of some cyanoazulenes.

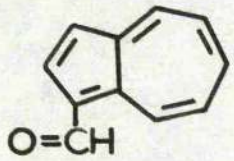
BI 12 Reactions of Azulenes with Aldehydes: Summary

The findings of this section may be summarised by saying that azulenes react readily with aldehydes providing that, in most cases, there is (i) strong acid available for catalysis and/or entry into the reaction product, and (ii) the carbonyl carbon atom is not deactivated by the proximity of an electron releasing group in the molecule. The subsequent course of the reaction, after initial electrophilic attack by the aldehyde at the 1(3)- position of the azulene, will depend on the nature of the aldehyde, and on the degree of alkylation of the azulene nucleus. These results are summarised by the reactions of guaiazulene shown in Fig. 4. In considering the preferred course of reaction for any given azulene with any given aldehyde, the factors discussed in the foregoing text must be taken into account.

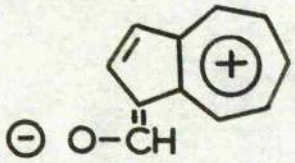
BII 1(3)-Formylazulenes

BII 1 Introduction

The 1(3)-formylazulenes constitute an interesting class of compounds, since it is to be expected that modern concepts of the structure of the azulene nucleus, involving dipolar resonance forms, will be reflected in a modification of the properties of the formyl group. Hence 1-formylazulene (49a) will receive a considerable contribution to its ground state from polar structures such as (49b). The chemical and physical data discussed in this section may be satisfactorily interpreted on the basis of this idea.



(49a)



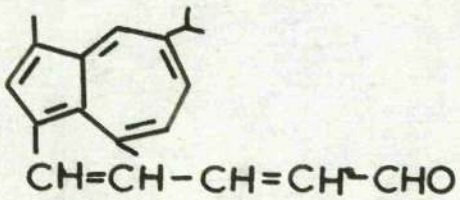
(49b)

The methods of synthesis of 1-formylazulenes are briefly reviewed elsewhere (AVII 6). The most convenient preparative method is undoubtedly by the reaction of the appropriate azulene with ethyl orthoformate and perchloric acid, with subsequent hydrolysis of the resulting 1(3)-ethoxymethylene-azulenium perchlorate (see (BIII 3)). This is only applicable, however, to azulenes with substituents that are sufficiently electron releasing to allow isolation of the 1(3)-ethoxymethyleneazulenium salt. Where this method fails, application of the Vilsmeier reaction[156] gives the desired products in high yield.

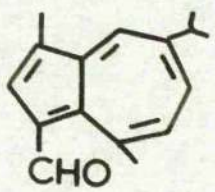
BII 2 Infra-Red Spectra

Since there is greater interaction between the carbonyl group and the π electrons of the nucleus in 1-acylazulenes than in acylated benzenoid hydrocarbons, the infra-red C:O stretching frequencies of the 1-formylazulenes are found to be abnormally low. Comparitive data are shown in Table 10, where it may be seen that there is a drop of 55-60 cm.$^{-1}$ in the C:O stretching frequency of 1-formylazulene compared with that of 6-formyl-4,8-dimethylazulene or 1-naphthaldehyde. In the latter compounds, there is no potential aromatic sextet in the vicinity which can be developed by polarisation of the carbonyl bond. A further reduction in frequency is noticed when the azulene nucleus carries electron releasing substituents (c.f. 3-formylguaiazulene and 1-formyl-4,6,8-trimethylazulene with 1-formylazulene).

It emerges that an abnormality of the carbonyl stretching frequency of an alkylated 1-formylazulene is correlated with its failure to condense with azulenes in the presence of perchloric acid (see (BIII 2)). The comparitively high carbonyl stretching frequency of 5-(guaiazulen-3-yl)penta-2,4-dienal (50), lies within the range of those of the simple polyene aldehydes, so there is practically no trans-



(50)



(51)

Aldehyde	Frequency($cm.^{-1}$)	Ref.
1-Formylazulene	1645	DI
1,3-Diformylazulene	1647	183
3-Formylguaiazulene	1610	183
1-Formyl-4,6,8-trimethylazulene	1618	Cv5
1-Formyl-4,8-dimethyl-6--phenylazulene	1631	Cv6
1-Formyl-4,8-dimethyl-6--methoxyazulene	1618	Cv7
1-Formyl-4,6-diphenyl-8--methylazulene (a)	1629	Cv8
1-Formyl-7-isopropenyl-4--methylazulene	1658(b)	70
6-Formyl-4,8-dimethylazulene	1705(b)	70, 184
1-Naphthaldehyde	1700(c)	180
2-Naphthaldehyde	1698(c)	180
5-(Guaiazulen-3-yl)penta-2,4--dienal	1668	176
$CH_3(CH{=}CH)_nCH{=}CH.CHO$ (n=2-7)	1677-1664(c)	185

Table 10 Infra-Red C:O stretching frequencies of azulene aldehydes in Nujol.

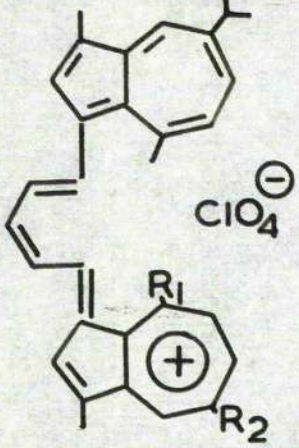
Notes: (a) and/or 1-Formyl-6,8-diphenyl-4-methylazulene

(b) in CS_2

(c) in $CHCl_3$

mission of the abnormal effect due to the polarisable azulene nucleus along a conjugated chain. The aldehyde (50), in contrast to 3-formylguaiazulene (51), readily condenses with

guaiazulene, and with 1-methylazulene, in the presence of perchloric acid, to give the salts (52) and (53) respectively[176].

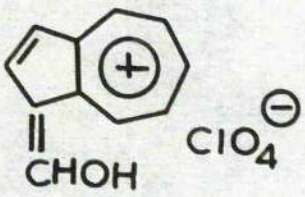


(52) R_1 = Me R_2 = isopropyl

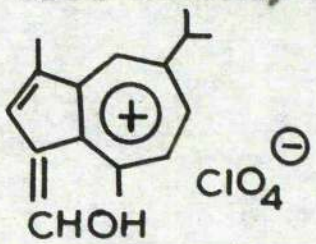
(53) $R_1 = R_2 = H$

BII 3 Chemical Properties

In accordance with the formulation of their structure, as typified by (49), the 1-formylazulenes are readily soluble in dilute acids, and form yellow crystalline 1-hydroxymethyleneazulenium salts. Thus 1-formylazulene (49) and 3-formylguaiazulene (51), when dissolved in acetic acid and treated with perchloric acid, deposit the crystalline salts (54) and (55) respectively (CIII 1, CIII 2). The product (55) from guaiazulene is the more stable, owing to



(54)



(55)

the greater basicity conferred by the electron releasing alkyl substituents. These salts are readily hydrolysed by water to the corresponding 1-formylazulenes, and they closely resemble the 1-ethoxymethyleneazulenium salts prepared by condensation of azulenes with ethyl orthoformate and strong

acid (BIII 4).

On heating in a strong acid solution, 1-formylazulenes eliminate the aldehyde group, as depicted for guaiazulene in Fig. 5. The hydrocarbons cannot be isolated from the lower members of the series, such as 1-formylazulene, by this procedure, because the free azulene produced, immediately

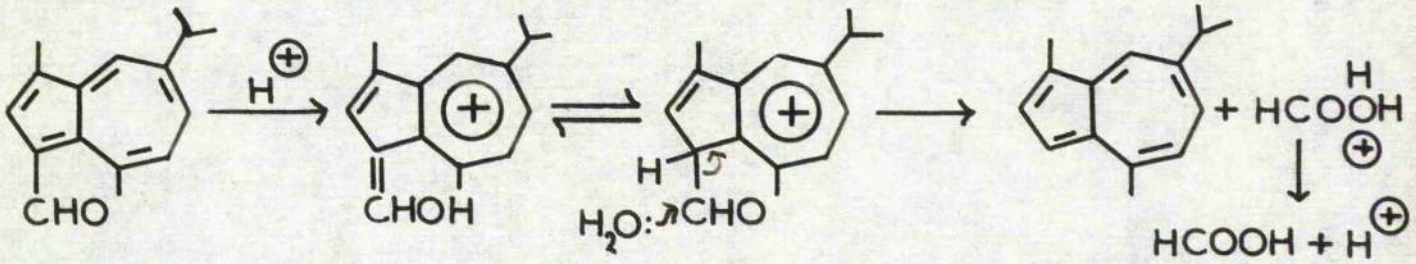
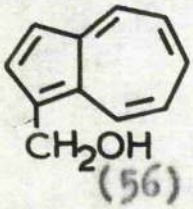


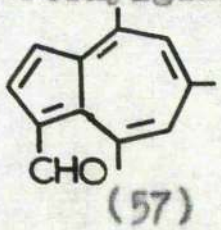
Fig. 5 Deformylation of 3-formylguaiazulene in acid solution.

undergoes condensation with the remaining 1-formylazulene to form a 1,1'-azulenylmethyleneazulenium salt (e.g. (CIX 8)).

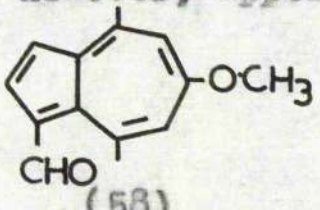
It has been reported[71] that 1-formylazulenes fail to undergo the Cannizzaro reaction or the benzoin condensation, or to oxidise to the corresponding carboxylic acids. The abnormality of behaviour of the aldehyde function increases with alkylation, which is in agreement with the above findings (BII 2). Thus 3-formylguaiazulene does not react[148] with Grignard reagents, whereas 1-formylazulene does[71]. With lithium aluminium hydride, 1-formylazulene is reduced to the alcohol (56)[164]. 3-Formylguaiazulene, however, appears[148]



(56)



(57)



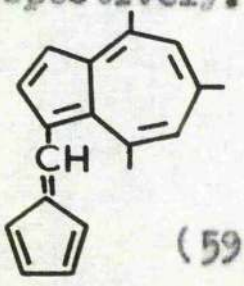
(58)

to suffer nucleophilic attack on the azulene nucleus, and no useful product can be isolated.

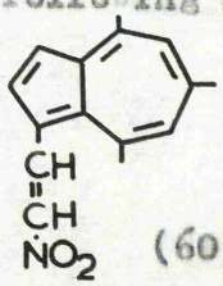
It appears that the position of alkylation of the azulene nucleus has a marked effect on the reactivity of the carbonyl group, for 1-formyl-4,6,8-trimethylazulene (57) behaved[71] like 1-formylazulene in its reactions with Grignard reagents and lithium aluminium hydride.

1-Formylazulenes all give normal carbonyl derivatives such as oximes and semicarbazones[71,148,72], and the majority also undergo Wolf-Kishner reduction to the corresponding 1-methylazulene (e.g. (DII), (DIV)), but 4,8-dimethylazulenes show anomalous behaviour. Thus the aldehydes (57) and (58) yielded no useful product under the conditions of the Wolf--Kishner reduction (DXXII, DXXIII).

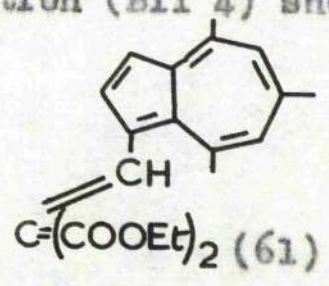
The carbonyl group of 1-formylazulenes will undergo condensation with an active methylene group. 1-Formylazulene and 1-formyl-3-methylazulene will, in effect, condense with the 3-methylene group of an azulenium cation (BIII 2). 1-Formyl-4,6,8-trimethylazulene has been shown[71] to condense with cyclopentadiene, nitromethane, diethylmalonate, and acetophenone to yield the products (59) (60), (61) and (37) respectively. The following section (BII 4) shows that it



(59)



(60)

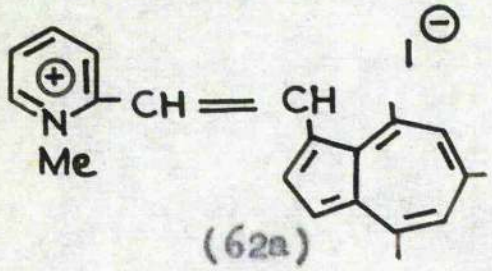


(61)

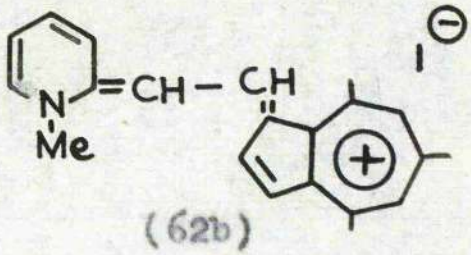
will also condense with heterocyclic quarternary ammonium salts which contain a reactive methyl group.

BII 4 Condensations with Heterocyclic Quarternary Ammonium Salts and Properties of the Resulting Dimethinecyanine Salts

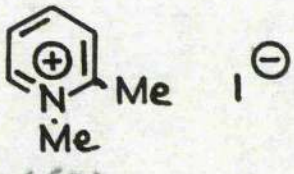
When 1-formyl-4,6,8-trimethylazulene and a heterocyclic quarternary ammonium salt with a reactive methyl group are boiled together for a short time in ethanol, with a small quantity of piperidine, a novel type of dimethinecyanine salt is formed. This reaction is exemplified by the formation of (62), which results when 1-formyl-4,6,8-trimethylazulene is treated with 1,2-dimethylpyridinium iodide (63) and piperidine. Resonance can occur between (62a) and (62b), and it follows



(62a)

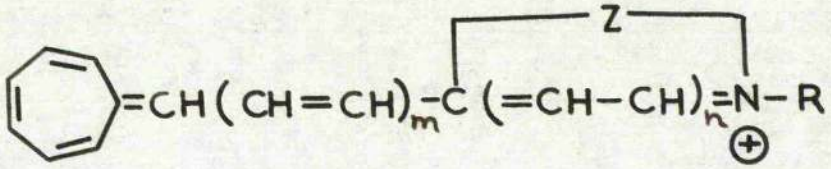


(62b)

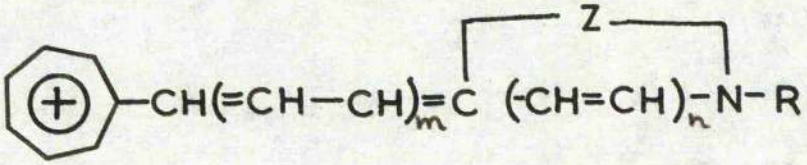


(63)

that this series, exemplified by (62), constitute one of several novel classes of cyanine dyes derived from the parent hypothetical structure (64) (n = 0 or 1; m = 0, 1, 2 etc.; Z is residue of a heterocyclic nucleus). Structurally they occupy an intermediate position between the cyanine dyes in



(64a)



(64b)

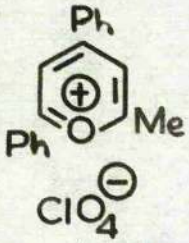
which the extreme resonance forms of the cation involve tertiary and quarternary nitrogen, and the all carbon 1,1'-azulenylmethyleneazulenium salts (BIII), whose cationic resonance is between two seven membered rings.

The heterocyclic compounds whose quarternary salts reacted with 1-formyl-4,6,8-trimethylazulene were 2- and 4-methylpyridine and quinoline, 2-methylbenzoxazole and benthiazole, and 2-methyl and 2,4-dimethylthiazole.

Other hypothetical series of salts suggest themselves, in which the nitrogen atom is replaced by other heteroatoms such as sulphur or oxygen. However, in an experiment in which a quantity of 1-formyl-4,6,8-trimethylazulene, 2,4-diphenyl-6-methylpyrylium perchlorate (65), piperidine, and ethanol were heated together, the expected product (66) was not formed.

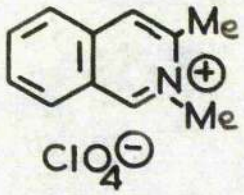
1-Formylazulene, 1-formyl-3-methylazulene, and 3-formylguaiazulene react in the same way with heterocyclic

quarternary ammonium salts[186]. Comparing the series derived from different 1-formylazulenes, it is found that alkylation of the azulene nucleus lowers, but does not completely suppress the carbonyl activity of 1-formylazulene. Thus no products could be isolated after treating 2,3-dimethylisoquinolinium perchlorate (67) with either 1-formyl-4,6,8-trimethylazulene or 3-formylguaiazulene, or after treating

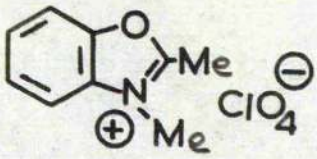


(65)

(66)



(67)



(68)

2,3-dimethylbenzoxazolium perchlorate (68) with 3-formylguaiazulene. This contrasts with the behaviour of 1-formylazulene and 1-formyl-3-methylazulene[186].

Table 11 shows the visible absorption maxima for these cyanine dyes. The spectra consist in all cases of a broad band devoid of fine structure.

Table 12 shows the displacement of λ max. for the compounds in Table 11, each one being calculated from the corresponding azulene derivative.

Alkylation of the azulenes nucleus produces a bathochromic displacement of λmax. in all cases (see Table 12), as is expected by analogy with the 1,1'-azulenylmethyleneazulenium salts (BIII). The average values of λ max. follow the expected sequence, i.e., 3-guaiazulenyl

	Cation	X	$\lambda_{max.}$	Log ε
1	1-Methyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}pyridinium	ClO_4	482m	4.59
2	1-Methyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}pyridinium	I	482m	4.59
3	3-Methyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}benzoxazolium	ClO_4	497	4.76
4	3,4-Dimethyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}thiazolium	ClO_4	499m	4.61
5	3,4-Dimethyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}thiazolium	I	499m	4.59
6	3-Methyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}thiazolium	ClO_4	499	4.61
7	1-Methyl-4-{2-(4,6,8-trimethylazulen-1-yl)vinyl}pyridinium	ClO_4	499	4.64
8	1-Methyl-4-{2-(4,6,8-trimethylazulen-1-yl)vinyl}pyridinium	I	499	4.64
9	3-Methyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}benzothiazolium	ClO_4	530m	4.74
10	1-Methyl-2-{2-(4,6,8-trimethylazulen-1-yl)vinyl}quinolinium	ClO_4	567	4.22
11	1-Methyl-4-{2-(4,6,8-trimethylazulen-1-yl)vinyl}quinolinium	I	572m	4.63
12	3-{2-(Azulen-1-yl)vinyl}-2-methylisoquinolinium	ClO_4	446m	4.53
13	2-{2-(Azulen-1-yl)vinyl}-1-methylpyridinium	ClO_4	469m	4.64
14	2-{2-(Azulen-1-yl)vinyl}-1-methylpyridinium	I	469m	4.63
15	2-{2-(Azulen-1-yl)vinyl}-3,4-dimethylthiazolium	I	481m	4.58
16	2-{2-(Azulen-1-yl)vinyl}-3-methylthiazolium	ClO_4	481	4.64
17	4-{2-(Azulen-1-yl)vinyl}-1-methylpyridinium	I	482	4.69
18	2-{2-(Azulen-1-yl)vinyl}-3-methylbenzoxazolium	ClO_4	491	4.79
19	1-{2-(Azulen-1-yl)vinyl}-2-methylisoquinolinium	ClO_4	493m	4.28
20	2-{2-(Azulen-1-yl)vinyl}-3-methylbenzothiazolium	ClO_4	514	4.78
21	2-{2-(Azulen-1-yl)vinyl}-1-methylquinolinium	ClO_4	522	4.79
22	4-{2-(Azulen-1-yl)vinyl}-1-methylquinolinium	I	541m	4.70
23	2-Methyl-3-{2-(3-methylazulen-1-yl)vinyl}isoquinolinium	ClO_4	462	4.54
24	1-Methyl-2-{2-(3-methylazulen-1-yl)vinyl}pyridinium	ClO_4	489m	4.65
25	3,4-Dimethyl-2-{2-(3-methylazulen-1-yl)vinyl}thiazolium	ClO_4	500m	4.59
26	3-Methyl-2-{2-(3-methylazulen-1-yl)vinyl}thiazolium	ClO_4	502m	4.61
27	1-Methyl-4-{2-(3-methylazulen-1-yl)pyridinium	ClO_4	502m	4.71
28	3-Methyl-2-{2-(3-methylazulen-1-yl)vinyl}benzoxazolium	ClO_4	509	4.79
29	3-Methyl-2-{2-(3-methylazulen-1-yl)vinyl}benzothiazolium	ClO_4	533	4.80
30	1-Methyl-2-{2-(3-methylazulen-1-yl)vinyl}quinolinium	ClO_4	543	4.80
31	1-Methyl-4-{2-(3-methylazulen-1-yl)vinyl}quinolinium	I	563	4.71
32	2-{2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl}-1-methylpyridinium	ClO_4	509m	4.65
33	4-{2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl}-1-methylpyridinium	I	524m	4.72
34	2-{2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl}-3-methylthiazolium	ClO_4	525m	4.69
35	2-{2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl}-3-methylbenzothiazolium	ClO_4	550m	4.78
36	4-{2-(5-Isopropyl-3,8-dimethylazulen-1-yl)vinyl}-1-methylquinolinium	I	592m	4.72

m broad (X^- = anion)

Table 11 Visible absorption maxima of dimethinecyanine salts in methanol.

Compound No. See Table 11	$\lambda_{max.}$ (Cm^{-1})	Azulene Componant	Ref.
1	+13	4,6,8-trimethylazulen-1-yl	CIV 1
2	+13	"	CIV 2
3	+6	"	CIV 3
4	+18	"	CIV 4
5	+18	"	CIV 5
6	+18	"	CIV 6
7	+17	"	CIV 7
8	+17	"	CIV 8
9	+16	"	CIV 9
10	+45	"	CIV 10
11	+31	"	CIV 11
23	+16	3-methylazulen-1-yl	186
24	+20	"	"
25	+19	"	"
26	+21	"	"
27	+20	"	"
28	+18	"	"
29	+19	"	"
30	+21	"	"
31	+22	"	"
32	+40	guaiazulen-3-yl	"
33	+42	"	"
34	+44	"	"
35	+36	"	"
36	+51	"	"

* Calculated in each case from the corresponding derivative of azulene.

Table 12 Effect on visible absorption maxima of dimethinecyanine salts of alkylation of azulene nucleus.

3-methylazulen-1-yl 4,6,8-trimethylazulen-1-yl, but quantitatively there is a wide divergence from the mean values among individual compounds in this series.

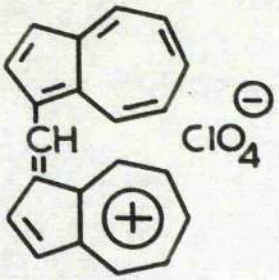
For each series with the same azulene nucleus (see Table 11) the absorption maximum shifts to longer wavelengths as the heterocyclic component is changed, in the order 3-isoquinoline, 2-pyridine, 2-(4-methylthiazole), 2-thiazole, 4-pyridine, 2-benzoxazole, 1-isoquinoline, 2-benzothiazole, 2-quinoline, 4-quinoline. The one exception to this is 3-methyl-2-(2-(4,6,8-trimethylazulen-1-yl)vinyl)benzoxazolium perchlorate, which precedes the compound derived from 2-(4-methylthiazole) and 1-formyl-4,6,8-trimethylazulene by 2 mμ. in order of increasing wavelength.

A few compounds of the same type have been reported from the condensation of azulenes with 2-formylmethylene compounds containing a heterocyclic nitrogen atom, in the presence of phosphorus oxychloride[187].

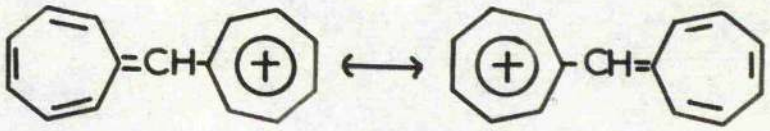
BIII 1,1'-Azulenylmethyleneazulenium Salts

BIII 1 Introduction

These compounds, of which the 1,1'-azulenylmethylene-azulenium cation of (7) represents the parent system, are members of a new class of all carbon polymethine dye-salts, based formally on the hypothetical cation (69). They represent the only known class of polymethine dye-salts whose cations certain carbon and hydrogen alone, and are



(7)



(69)

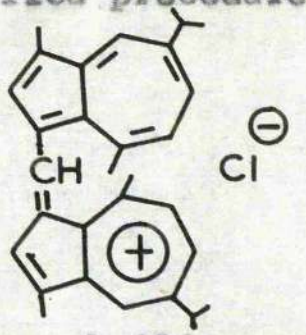
stable salts, showing very intense absorption ($\varepsilon \sim 10^5$) at long wavelengths (λ max. $>$ 615 mμ.).

It had been reported[153] (without experimental details) that 1-formylazulene underwent self-condensation, with deformylation in the presence of phosphorus oxychloride, to give 1,1'-azulenylmethyleneazulenium chloride ((7); ClO_4 replaced by Cl). Other workers[188,189,190] reported that this compound, and the perchlorate (7) could be prepared by condensing azulene with ethyl orthoformate in the presence of the appropriate acid, and the structure was confirmed[189] by an independent synthesis of the chloride by condensing 1-formylazulene with azulene in the presence of methanol and hydrochloric acid.

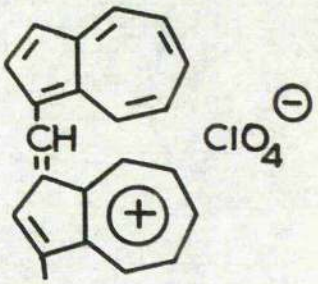
In view of the theoretical interest of this system, its relationship to other molecules containing an azulenium structure, and its occurrence in reactions of 1(3)-methylazulenes involving hydride ion transference (BV), a fuller investigation was carried out on its properties and methods of synthesis, both for the parent compound (7), and its alkylated derivatives.

BIII 2 Synthesis by Condensation of Azulenes with 1-Formylazulenes in the Presence of Strong Acids

This procedure involves the same kind of reaction as the condensations of other aromatic aldehydes with azulenes (BI 1, BI 2). It has been reported[148] that 3-formylguaiazulene condenses with guaiazulene in ether containing anhydrous hydrogen chloride to form 3,3'-guaiazulenylmethyleneguaiazulenium chloride (70), which, however, was not isolated. Using the modified procedure (see BI 2) of carrying out the



(70)



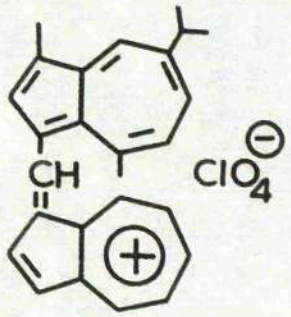
(71)

condensation in a boiling solution of perchloric acid in acetic acid, several of the dye-salts could be prepared. 1-Formylazulene and azulene readily gave the salt (7) (CII 1), and 1-formylazulene with 1-methylazulene gave 1-(3-methylazulen-1-yl)methyleneazulenium perchlorate (71) (CII 2). The product of condensation of 1-formyl-3-methylazulene with azulene[191] was identical with (71), which is in agreement with the formulation of these structures as resonance hybrids.

However, the method is not of general applicability. While 1-formylazulenes and 1-formyl-3-methylazulene condensed with all azulenes, the more highly alkylated 1-formylazulenes did not. Thus 3-formylguaiazulene would not condense with

azulene or guaiazulene, and 1-formyl-4,6,8-trimethylazulene gave products which were very impure. This deactivation is to be attributed to the electron releasing effect of the alkyl groups, which lowers the electrophilic character of the carbonyl carbon atom (see (BII 3)).

In certain cases the desired products were obtained by exchanging the roles of the azulene nuclei. Thus, while 3-formylguaiazulene failed to condense with azulene, 1-formylazulene condensed smoothly with guaiazulene to give the salt (72) (CII 3). Exchange of the azulene nuclei in



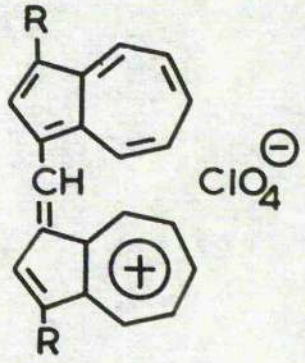
(72)

this manner assists the desired reaction in two ways, (i) the electrophilic character of the carbonyl carbon atom is increased, and (ii) the nucleophilic character of the 1(3) position(s) of the other azulene nucleus is increased. This circumvention failed, however, in the attempted preparation of salts such as (21) and (26), both of whose azulene components give rise to unreactive aldehydes.

BIII 3 Synthesis by Condensation of Azulenes with Ethyl Orthoformate in the Presence of Strong Acids

This method was investigated as a possible general route to the symmetrical 1,1'-azulenylmethyleneazulenium

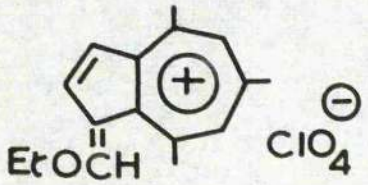
perchlorates. The reported result from using azulene[188,189,190] was confirmed, but it was also further found that the type of product depends on the degree of alkylation of the azulene nucleus. Azulene and 1-methylazulene with either stoichiometric quantities or an excess of ethyl orthoformate, in the presence of perchloric acid, gave almost quantitative yields of the dye-salts (7) and (73) respectively (CV 1, CV 2).



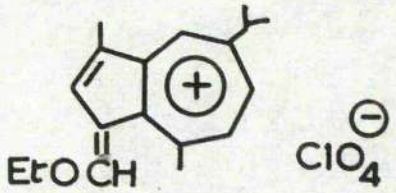
(7) R = H

(73) R = Me

In contrast, 4,6,8-trimethylazulene with perchloric acid, and a large excess (800%) of ethyl orthoformate in ethanol gave 1-ethoxymethylene-4,6,8-trimethylazulenium perchlorate (74) in 94% yield (CV 5). Guaiazulene similarly gave (75)[191].



(74)



(75)

Other conditions remaining the same, the proportion of ethyl orthoformate determines the yield. Results of experiments in which the excess of ethyl orthoformate was varied are shown in Table 13.

These observations may be plausibly interpreted by

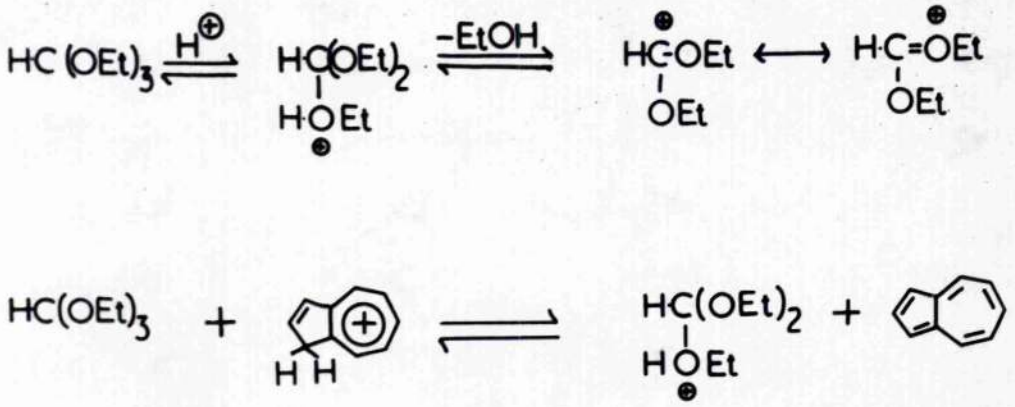


Fig.6.

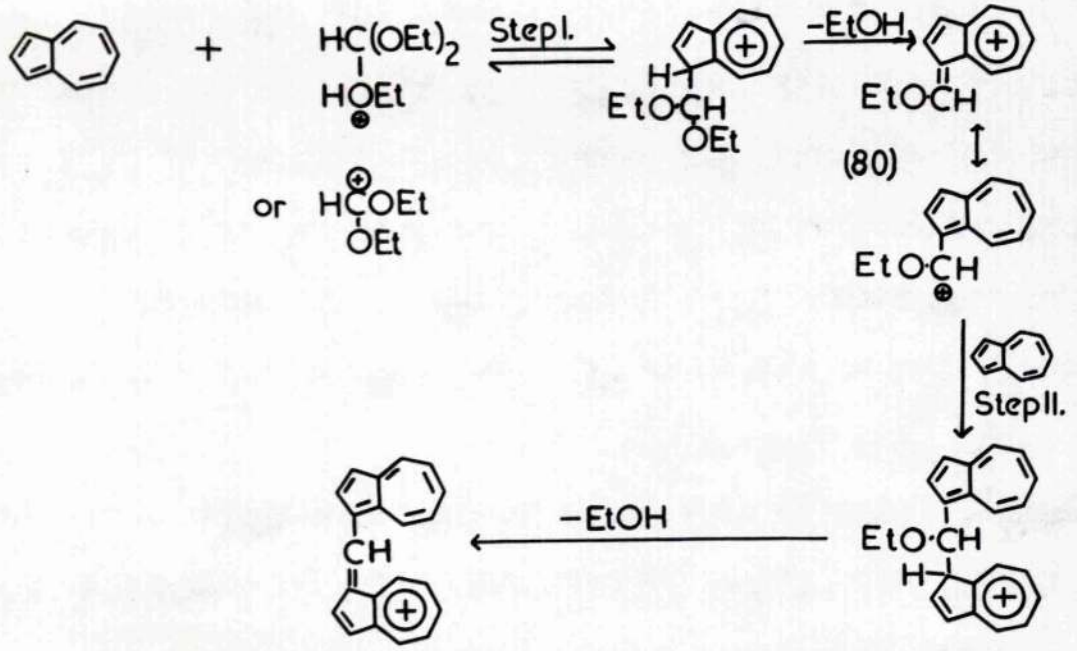


Fig.7. Reaction of azulene with ethyl orthoformate in the presence of strong acid.

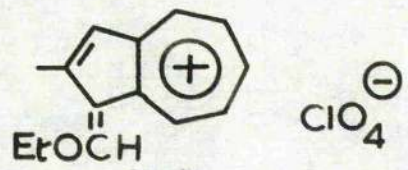
Azulene (A)	% Excess of $H{\cdot}C(OEt)_3$ (B)	Molar ratio B:A	% Yield of (74) or (75)	Ref.
4,6,8-trimethyl-azulene	620	7.2:1	5	CV 5
" " "	800	9:1	94	CV 5
Guaiazulene	100	2:1	0	191
" "	400	5:1	55	191
" "	800	9:1	90	191

Table 13 Effect of an excess of ethyl orthoformate on yield of 1-ethoxymethyleneazulenium perchlorates.

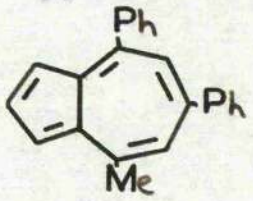
assuming that the function of the excess of ethyl orthoformate is to release the free azulene from the azulenium cation. The equilibrium shown in Fig. 6 is then set up. Azulene and 1-methylazulene are less basic than the more highly alkylated azulenes, and in a given acid solution there is therefore a higher concentration of free azulene, so that the concentration of ethyl orthoformate required for reaction is not of the same importance.

Summarising the results of the reactions of azulenes with ethyl orthoformate and perchloric acid, azulene and 1-methylazulene gave the symmetrical dye-salts (7) and (73) respectively (CV 1, CV 2). 2-Methylazulene (CV 3), 1,2-dimethylazulene (CV 4), 4,6,8-trimethylazulene (CV 5), guaiazulene[191], 4,8-dimethyl-6-phenylazulene (CV 6), 4,8-dimethyl-6-methoxyazulene (CV 7), and 4,6-diphenyl-8-methyl-

azulene (CV 8), all gave the corresponding 1(3)-ethoxymethyleneazulenium perchlorates. 1-Ethoxymethylene-2--methylazulenium perchlorate (76) could not be isolated as a pure crystalline solid in sufficient quantity for characterisation. Notably, 4,6-diphenyl-8-methylazulene (77) did not give a pure product (CV 8), and it seems likely

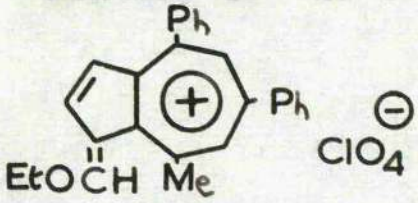


(76)

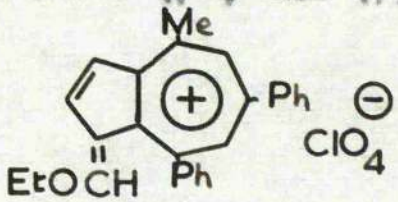


(77)

that a mixture of the two possible salts (78) and (79) are



(78)



(79)

formed.

A typical reaction scheme which will allow a rational interpretation of these condensations is outlined in Fig. 7.

For the reactions with azulene and 1-methylazulene, the intermediate corresponding to (80) cannot be isolated. Further alkylation of the azulene nucleus, however, lowers the electrophilic character of the methine carbon atom of the 1-ethoxymethyleneazulenium cation (80). This inhibits further reaction with an excess of the azulene, and (80) is the reaction product.

These 1(3)-ethoxymethyleneazulenium salts are readily

hydrolysed by water to the corresponding aldehydes, and this provides the most convenient synthesis yet devised of 1-formylazulenes from azulenes.

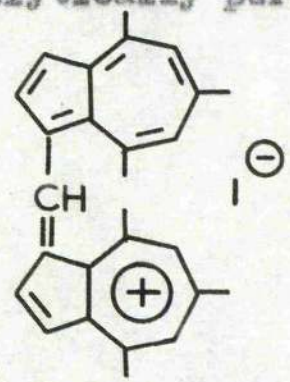
3-Ethoxymethyleneguaiazulenium (75) and 1-ethoxymethylene--4,6,8-trimethylazulenium perchlorate (74) react at once with azulenes in alcohol or acetonitrile to form 1,1'-azulenylmethyleneazulenium perchlorates, e.g. (CVI 1, 2, and 3). No appreciable reaction took place, however, in the presence of perchloric acid. This is presumably to be traced to the conversion of the azulene into the unreactive azulenium cation, and is parallel to the noted absence of reaction of certain azulenes with ethyl orthoformate and acid unless a large excess of ethyl orthoformate is present.

Since the azulenes whose 1-aldehydes fail to condense with azulenes in the presence of perchloric acid are those which form isolable 1-ethoxymethyleneazulenium perchlorates, the two limited methods of preparation together constitute one general synthetic method for the dye-salt series.

The 1(3)-ethoxymethyleneazulenium salts closely resemble the corresponding 1-hydroxymethyleneazulenium salts (BII 3). The perchlorates crystallise readily as golden yellow plates or needles. The visible spectrum consists of a single band in the range 400-450 mμ. (CV 6, CV 7).

1-Ethoxymethylene-4,6,8-trimethylazulenium bromide was isolated by condensation of 4,6,8-trimethylazulene with ethyl

orthoformate in the presence of 50% (w/w) hydrogen bromide in acetic acid (CV 9). This product is extremely sensitive to hydrolysis by atmospheric moisture. The corresponding iodide was prepared by the reaction of the same mixture in the presence of an excess of sodium iodide (CV 10). This iodide is more stable to the atmosphere than the bromide, but is thermally unstable, and has a great tendency to undergo self condensation to the dye-salt (81), although this could not be isolated in an analytically pure condition.



(81)

BIII 4 1,1'-Azulenylmethyleneazulenium Salts:- Other Synthetic Routes

The system (7) is formed in the course of several diverse reactions, which reflects its considerable resonance stability. These are briefly mentioned here for the sake of completeness, although they vary in their suitability as preparative methods, and are discussed in more detail in other sections.

Self-condensation of 1-Formylazulene in the Presence of Conc. Hydrochloric Acid

This method gave the parent perchlorate (7) in pure condition, although not in very high yield (CIX 8). It is

not applicable to highly alkylated azulenes since these undergo complete deformylation (see (BII 3)).

Condensation of Azulenes with α-Oxoaldehydes and Perchloric Acid

This appears to be generally applicable to the synthesis of symmetrical dye-salts in high yield (BI 7).

Condensation of Azulenes with β-Oxoaldehydes and Perchloric Acid

The parent dye salt (7) may readily be prepared by condensations in this category, but the highly alkylated symmetrical dye-salts can only be obtained in traces.

1,1'-Azulenylmethyleneazulenium perchlorate (7) has also been obtained by condensation of a 2-(azulen-1-yl)methylene ketone with azulene[176]. The scope of this procedure has not been explored, but it appears to parallel that of condensations of 1-formylazulenes with azulenes (BIII 2).

Dehydrogenation of 1,1'-Diazulenylmethanes

3,3'-Guaiazulenylmethyleneguaiazulenium perchlorate (21) has been obtained by dehydrogenation of 3,3'-diguaiazulenylmethane, using triphenylmethyl perchlorate, but the yield is unsatisfactory[192] (see BV 5).

Intermolecular Dehydrogenation of 1(3)-Methylazulenes

1(3)-Methylazulenes give dye-salts on treatment with very powerful electrophilic reagents such as triphenylmethyl perchlorate (BV 5). The reaction picture is complex and is

discussed in detail in section (BV 5).

BIII 5 Properties and Visible Spectra of 1,1'-Azulenylmethyleneazulenium Perchlorates

The spectra of these salts consists in each case of a single sharp intense absorption band. The positions of λmax. are shown in Table 14, (see Plates XIII and XIV). The following generalisations are apparent, (i) Alkylation of one or both azulene nuclei always produces a bathochromic displacement of λmax., whose magnitude depends upon the position(s) and number of substituents. (ii) For the series of dye-salts ($Y\overset{+}{=}CH-Z$ $Y-\overset{+}{C}H-Z$ $Y-CH=\overset{+}{Z}$) ClO_4^-, in which the nucleus Y is the same, λmax. shifts progressively to longer wavelengths as Z changes in the order azulen-1-yl, 4,6,8-trimethylazulen-1-yl, 3-methylazulen-1-yl, guaiazulen-3-yl. If the dye-salts containing an unsubstituted azulene nucleus are taken as standards, the shifts associated with each substituent or group of substituents are as follows, the last one being obtained by the difference of the two preceding ones:

4,6,8-trimethyl	+ 9 mμ.
3-methyl	+ 16 "
5-isopropyl-3,8-dimethyl	+ 26 "
5-isopropyl-8-methyl	+ 10 "

(iii) The shifts are additive, and agreement between calculated and observed values of λmax. is good for most

Azulene Nuclei in 1,1'-azulenylmethyleneazulenium perchlorate(a)		λ max. (mμ.)	Log ε	Ref.
Azulene	Azulene	618	5.08	CII 1 CV 1
Azulene	4,6,8-trimethylazulene	627(b)	5.00	CVI 1
Azulene	1-methylazulene	634	5.02	CII 2
4,6,8-trimethylazulene	4,6,8-trimethylazulene	640	4.94	CVI 2
Azulene	Guaiazulene	644	4.98	CII 3
4,6,8-trimethylazulene	1-methylazulene	644	5.03	191
1-methylazulene	1-methylazulene	652	5.01	CV 2
guaiazulene	4,6,8-trimethylazulene	653	4.93	CVI 3
guaiazulene	1-methylazulene	663	4.97	191
guaiazulene	guaiazulene	680	5.08	191

Table 14 Visible absorption maxima of 1,1'-azulenylmethyleneazulenium perchlorates in acetic acid.

Notes: (a) linked through 1- or 3- position, whichever is available.

(b) in acetic acid containing 4% (v/v) acetonitrile.

salts, but λ max. (observed) is greater than that predicted in the case of the symmetrically alkylated dye-salts. A comparison of the observed values of λmax., and those predicted from the above data is shown in Table 15.

The abnormally high values of Δλmax. for the symmetrically

Azulene nuclei in 1,1'-Azulenylmethylene-azulenium perchlorate[a]		Predicted position of λmax. (mμ.) [b]	λmax. observed (mμ.)	Ref.
4,6,8-trimethylazulene	1-methylazulene	618+9+16 = 643	644	191
" "	guaiazulene	618+9+26 = 653	653	CVI 3
guaiazulene	1-methylazulene	618+26+16 = 660	663	191
" "	guaiazulene	618+26+26 = 670	680	191
4,6,8-trimethylazulene	4,6,8-trimethylazulene	618+9+9 = 636	640	CVI 2
1-methylazulene	1-methylazulene	618+16+16 = 650	652	CV 2

Table 15 Comparison of observed and predicted positions of visible absorption maxima of 1,1'-azulenylmethyleneazulenium perchlorates in acetic acid.

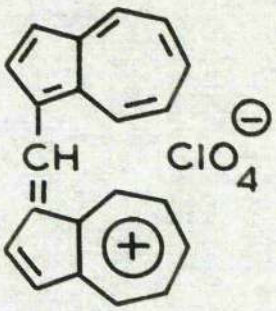
Notes: (a) Azulene nuclei linked through 1- or 3-position.

(b) Calculated as explained in the text above.

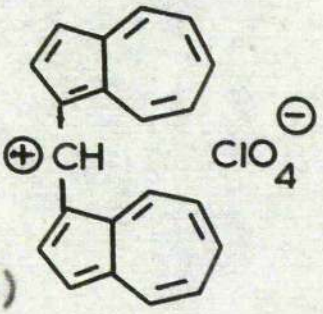
alkylated salts may be due to steric hindrance. Such effects cause discrepancies in the Plattner additivity rules for alkylated azulenes (see (AV)), but this would not explain the slightly high values for the two salts containing the 1-methylazulene nucleus.

The dominating chemical feature of this series is the electrophilic character of the methine carbon atom. This follows from the fact that in one of the limiting resonance forms (7a) of the dye salt (7), the positive charge resides

on this atom.

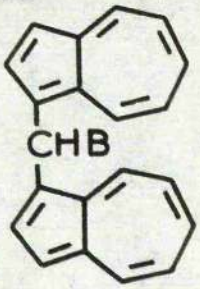


(7)



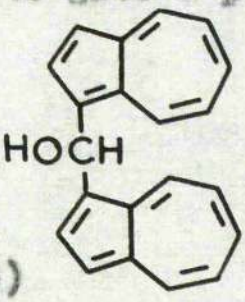
(7a)

The parent dye salt (7) has been reported[153] (without experimental details) to react with bases such as methoxides amines, and cyanides, to yield products of type (82). It is also reported[189] to react with alkali to give a pale yellow



(82)

B=-OMe,-NHR, -CN.



(83)

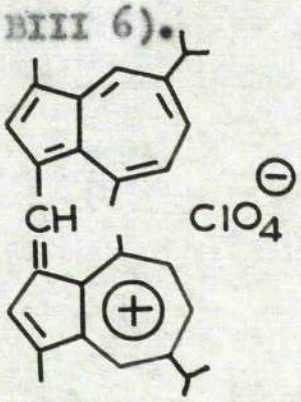
solid, m.p. 73-76°. This could not be purified further as it polymerised during attempted recrystallisation. It was suggested by the authors[189] that this may be the carbinol (83), although it is hard to see why such a compound, containing two intact azulene nuclei, should be practically colourless.

In common with some of the 1-(R-methylene)azulenium salts (81), 1,1'-azulenylmethyleneazulenium salts are readily reduced by lithium aluminium hydride. 3,3'-Diguaiazulenylmethane (84) has been obtained in this way from the symmetrical dye salt (21)[178].

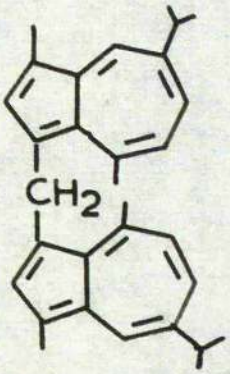
The present work has also shown that a nucleophilic

attack, by another azulene molecule, on the methine carbon atom is possible, with subsequent replacement of one (or both) of the nuclei (BIII 6).

(21)



(84)



When dissolved in organic solvents, these dye-salts have an intense blue colour. Their solubility varies considerably throughout the series, depending on the degree of alkylation. The parent 1,1'-azulenylmethyleneazulenium perchlorate (7), and the corresponding 3-methyl (71), and 3,3'-dimethyl (73) derivatives are only just sufficiently soluble in acetic acid for spectra determination (~ 1mg./500 ml.), and, for recrystallisation, a large volume of acetonitrile is required. The more highly alkylated ones (e.g. (21)) however, may conveniently be recrystallised from acetic acid, and are too soluble in acetonitrile for this purpose. The corresponding chlorides[191] are more soluble than the perchlorates, and are readily soluble in water.

After prolonged boiling in conc. hydrochloric acid solution, the highly alkylated dye-salts have been shown to cleave and regenerate the free azulenes. This is discussed in section (BIII 7).

XIII 6 Nucleophilic Attack of 1,1'-Azulenylmethylene-azulenium Salts by Azulenes

While investigating the reaction between azulenes and triarylmethylperchlorates (see (IV 5)), it became necessary to determine whether any interchange was possible in solution between azulene nuclei in a 1,1'-azulenylmethyleneazulenium salt and a free azulene present in excess. This has been found to be so, and if a dye-salt is refluxed for some time with an azulene, analysis of the hydrocarbon remaining after reaction clearly shows the presence of a new azulene derived from the original dye-salt.

The spectrum of the recovered dye-salt shows a broadening of the curve on the expected side, but the position of the absorption maximum is not usually changed significantly. It is evident that although there is a distinct difference between the position of the absorption maximum of a dye-salt and its alkylated homologue (see Table 14), the position of one will not show any significant displacement towards that of another until a nearly 1:1 proportion has been reached. A displacement of the absorption curve as a whole may often be seen, however, coupled with a lowering of the extinction coefficient (e.g. see Plate XV).

Quantitative conversion could not be achieved in any of the experiments conducted. This may be due in part to the low solubility of the dye-salts, but on the other hand there was no apparent improvement in the case of the more highly

alkylated dye-salts, which are slightly more soluble, nor when acetonitrile was used as solvent, nor when the reaction time was considerably extended.

The results of these experiments are summarised in Table 16. To illustrate the meaning of the term "% conversion", the following example is worked out:-

In experiment CX2, 1,1'-azulenylmethyleneazulenium perchlorate (0.000136 moles) and guaiazulene (0.000556 moles) were boiled together in acetic acid. If both azulene nuclei in the dye-salt were replaced by guaiazulene, the resultant hydrocarbon mixture would consist of (0.000556 -(2 x 0.000136) = 0.000284) moles of guaiazulene and (2 x 0.000136 = 0.000272) moles of azulene, which means 28.1% (w/w) of azulene. The composition of the mixture observed from the gas-chromatogram, however, is 4% (w/w). This represents a 14% conversion. The calculation was based on the most highly alkylated possible product in each case.

The last experiment (CX5) recorded in Table 16 is complicated by the fact that three kinds of azulene nucleus are present. If the dye-salt in this case was completely converted into 1-(3-methylazulen-1-yl)methylene-3-methyl azulenium perchlorate, the composition of the resultant hydrocarbon mixture would be azulene (22%) (w/w), 1-methylazulene (44%) and guaiazulene (34%). The observed composition (CX5) was azulene (15%), 1-methylazulene (40%), and guaiazulene (45%).

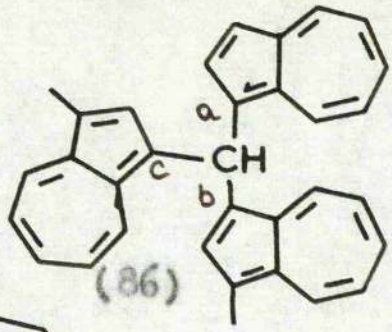
Reactants		Mole ratio azulene : dye-salt	Reflux time in acetic acid	% Conversion	Ref.
Azulene nuclei in 1,1'azulenyl-methylene-azulenium perchlorate	Azulene				
Azulene, 1-methyl-azulene	1-methyl-azulene	2.33	15 mins.	10	CX1
Azulene, 1-methyl-azulene	"	3.52	1 hr. (in aceto-nitrile)	19	CX1
Azulene, 1-methyl-azulene	"	3.30	2 hrs.	50	CX1
Azulene, azulene	4,6,8-tri-methyl-azulene	3.02	19 hrs.	35	CX3
Azulene, azulene	Guai-azulene	4.09	1.75 hrs.	14	CX2
1-methyl-azulene, 1-methyl-azulene	Guai-azulene	2.89	3 hrs.	16	CX4
Azulene, guaiazulene	1-methyl-azulene	3.80	2 hrs.	---	CX5

Table 16 Reaction of azulenes with 1,1'-azulenyl-methyleneazulenium perchlorates.

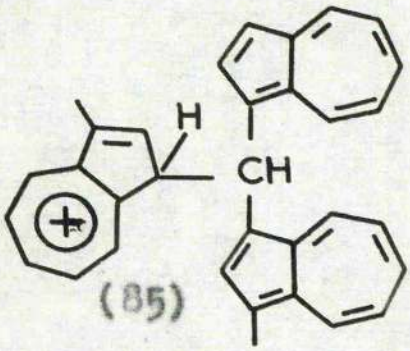
The only likely reaction scheme that can be envisaged, to interpret these data, involves a nucleophilic attack of the methine bridging carbon atom by the azulene molecule.

In experiment (CX1), for instance, the cation of the initial product presumably has structure (85).

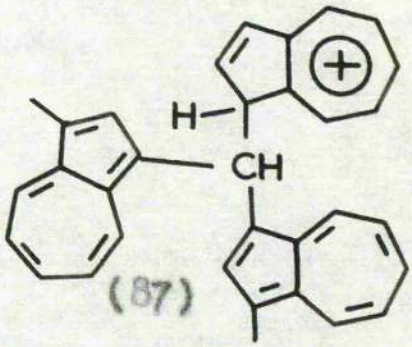
The next step necessary for elimination of the azulene



(86)

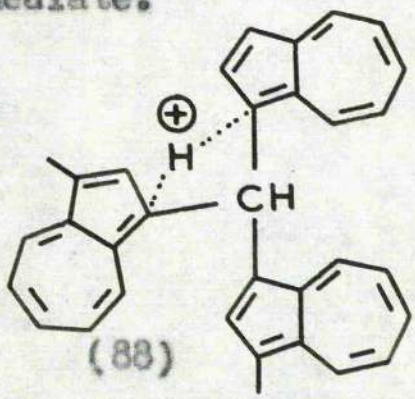


(85)

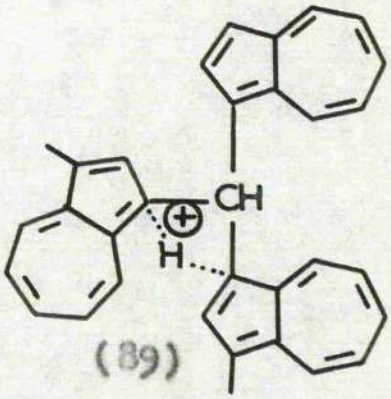


(87)

nucleus is the transfer of the proton of the attacking 1-methylazulene to an azulene nucleus, resulting in structure (87). This could occur either through the complete elimination of a proton, thus forming di(3-methylazulen-1-yl)-azulen-1-ylmethane (86) as an intermediate, or by an intra-molecular mechanism, perhaps forming structure (88) as an intermediate.



(88)



(89)

If the free triazulenylmethane (86) is formed, the second step of reprotonation, with subsequent cleavage of the azulene nucleus, would be suppressed by using an aprotic solvent. So the fact that the same reaction occurs when acetonitrile is used instead of acetic acid (CX1) would seem

to exclude this possibility.

A further point is that in the hypothetical triazulenylmethane (86), of the three sites (a, b, and c) for protonation which could lead to cleavage, (a) would be expected to be the least nucleophilic, by virtue of the 3-methyl substituents carried by the other azulene nuclei. Also, on statistical grounds, ignoring possible steric and electronic effects, there is only a 1 in 3 chance of protonation at this point. Many of the tripyrrylmethanes readily cleave under acid conditions, and the unsymmetrical ones cleave to give a single pair of reaction products. This has been explained by differing velocities for the various reactions[193], rather than the electronic effects of substituents on the readiness to assume the required transition state[194].

If any triazulenylmethanes were present in the reaction products they would probably have escaped detection. During the gas-chromatographic analyses, 3,3'-diguaiazulenylmethane was run, but was not eluted after 114 mins. at 200° (C.f. data for other azulenes in appendix). On the other hand if any appreciable quantity were present, one would expect it to have showed up by its relative slowness of elution from the column of alumina used in the process of isolation.

If the reaction of (CX1) proceeds through intramolecular transition states such as (88) or (89), then assuming that both are present and can give rise to two different pairs of

products, depending on which direction the proton moves in, there will be a 1 in 4 chance of replacement of azulene by 1-methylazulene on purely statistical grounds. This is less than the maximum amount of displacement observed (1 in 2), so that electronic and/or steric factors presumably play an important part.

To summarise; solutions of 1,1'-azulenylmethylene-azulenium perchlorates with an azulene have been found to suffer interchange of the azulene nuclei, and an equilibrium is probably set up. The reaction proceeds through an intramolecular mechanism. The factors determining the composition of the final mixture have not been fully elucidated, but there is no simple correlation with the degree of alkylation of the azulene nuclei.

BIII 7 Cleavage of 1,1'-Azulenylmethyleneazulenium Salts in Conc. Hydrochloric Acid Solution

Some 1,1'-azulenylmethyleneazulenium salts have been shown to cleave in acid solution (CIX). The results are summarised in Table 17. Table 18 shows the effect of acid on azulenes with electron-withdrawing substituents in the 1(3)-positions.

When 1-formylazulene is dissolved in conc. hydrochloric acid, a yellow solution results, which deposits yellow needles of 1-hydroxymethyleneazulenium chloride. The corresponding perchlorate was isolated and characterised as a rather

Azulene nuclei in 1,1'-azulenyl methylene azulenium perchlorate	Products after refluxing with conc. HCl		
	Hydrocarbon	λmax. of recovered dye-salt	Ref.
Azulene, Azulene	Nil	618 m.μ.	CIX1
1-Methylazulene, 1-Methylazulene	Nil	635 m.μ.	CIX2
Guaiazulene, Guaiazulene	Guaiazulene	Nil	CIX4
4,6,8-trimethyl-azulene, 4,6,8-trimethyl-azulene	4,6,8-trimethyl-azulene	Nil	CIX5
Guaiazulene, Azulene	Guaiazulene(97%) Azulene (3%)	Some at 618 m.μ. max. of bulk at 633 and 638 m.μ.	CIX6
Guaiazulene, 1-Methylazulene	Guaiazulene 82% 1-Methylazulene 18%	637 m.μ.	CIX7

Table 17 Effect of boiling conc. hydrochloric acid on 1,1'-azulenylmethyleneazulenium perchlorates.

1(3)Substituted azulene	Product after boiling with Conc. HCl	Ref.
1-Formylazulene	1,1'-azulenylmethylene-azulenium chloride (isolated as perchlorate)	CIX8
3-Formylguaiazulene	Guaiazulene	148
3-Acetyguaiazulene	"	"
3-Benzoylguaiazulene	"	"
3-Cyanoguaiazulene	"	"
3,3'-Diguaiazulenyl ketone	"	"
Oxime of 3-formylguaiazulene	"	"
1-Formylvetivazulene	Vetivazulene	72

Table 18 Effect of boiling conc. HCl on some 1(3)-substituted azulenes.

unstable salt (CIII 1). On warming, the mixture became deep purple, and addition of perchloric acid caused precipitation of 1,1'-azulenylmethyleneazulenium perchlorate (7). It is evident that as soon as any free azulene has been formed by deformylation, it at once condenses with the remaining 1-formylazulene in the manner described previously (BIII 2). This is in accordance with the previously noted reaction of azulene with ethyl orthoformate and strong acid (BIII 3), in which 1-ethoxymethyleneazulenium perchlorate cannot be isolated, owing to its immediate conversion to the dye-salt (7), irrespective of the proportions of the reactants.

The more highly alkylated azulenes, guaiazulene, and 4,6,8-trimethylazulene, however, do not condense with their

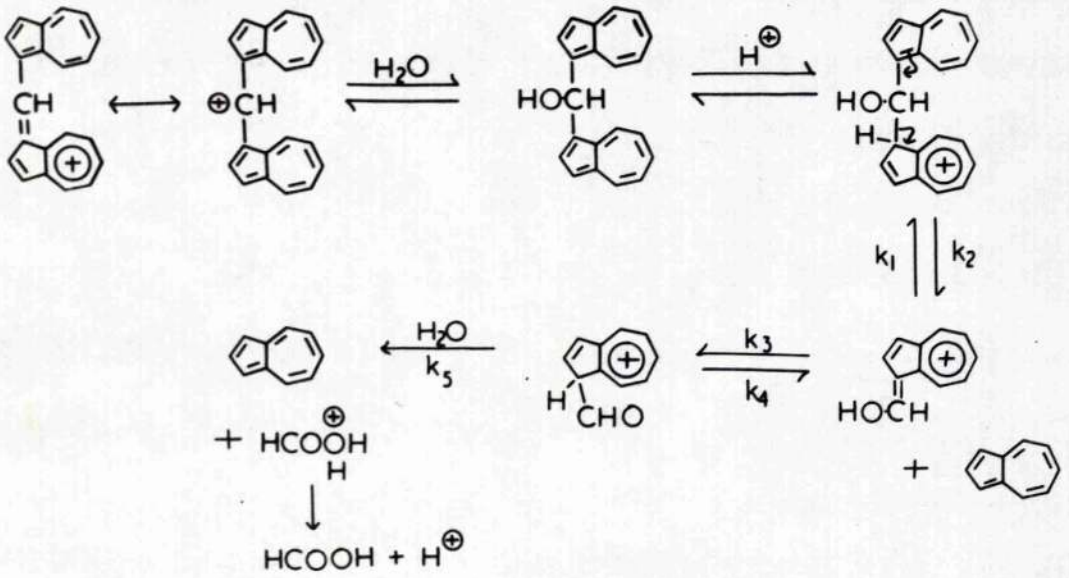


Fig. 8. Cleavage of 1,1'-azulenylmethyleneazulenium salts by conc. HCl.

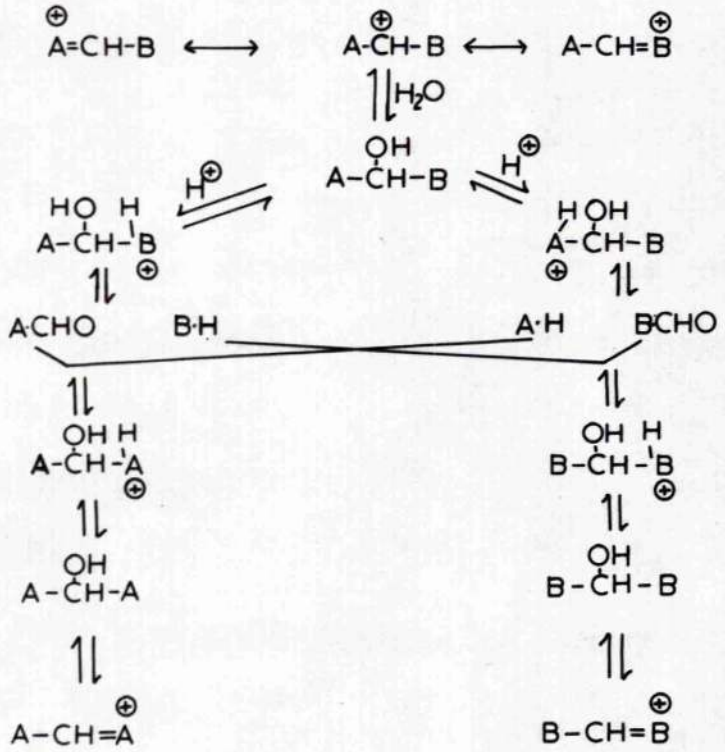


Fig. 9. Rearrangement of an unsymmetrical 1,1'-azulenylmethyleneazulenium salt in conc. HCl.

1-formyl derivatives (XIII 2), and so on boiling with conc. HCl, these 1-formylazulenes are entirely converted into the parent azulenes.

Bearing these facts in mind, the results summarised in Table 17 are susceptible to a rational interpretation. It seems probable that the initial step is one of hydrolysis by the water present, followed by protonation and cleavage according to the scheme outlined in Fig. 8.

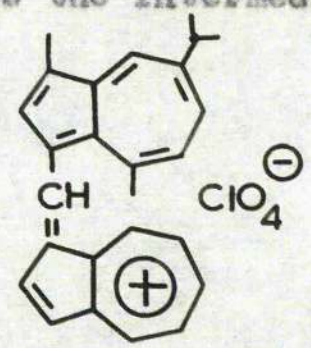
In the case of azulene itself, k_1 is much greater than k_3 and/or k_5, and $k_4 > k_2$. With guaiazulene and 4,6,8-trimethylazulene, however, the reverse holds, so that since the final deformylation step is irreversible and k_1 is practically zero, the symmetrical dye-salts from these azulenes are converted quantitatively into azulenes.

With an unsymmetrical dye-salt, there are two possible sites for protonation (neglecting others which can lead to no further reaction). Thus for the unsymmetrical dye-salt $\overset{+}{A}$=CH-B, the equilibrium scheme in Fig. 9 is established.

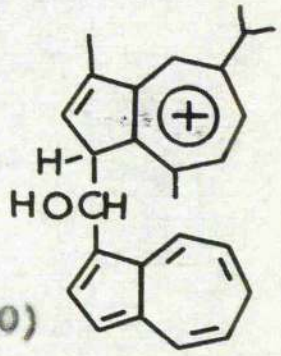
Assuming, for the moment, that both sites for protonation are equally probable, there are three possible dye-salts, and two possible hydrocarbons which may be produced in equilibrium, if the reaction velocities have a suitable relation to each other.

It is clear, however, that both sites are not equally favoured; in the dye-salt (72), for instance, the guaiazulene nucleus would be expected to be the most nucleophilic,

because of the inductive/hyperconjugative effect of the alkyl groups, and so, after hydrolysis, (72) should produce structure (90) as the intermediate.



(72)



(90)

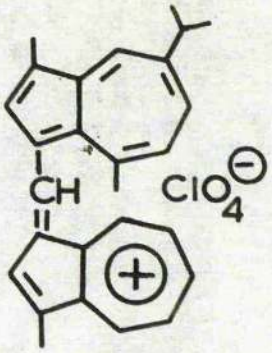
This would give guaiazulene, and 1,1'-azulenylmethylene-azulenium chloride (isolated as perchlorate (7)). Some azulene (3%) is produced however (see Table 17), and the bulk of the recovered dye-salt shows an absorption at 633 m.μ., which indicates contamination of the parent dye-salt (7) (λmax. 618 m.μ.) with the dye-salt (72) and/or 3,3'-guaiazulenylmethyleneguaiazulenium perchlorate (21). So the alternative reaction must have taken place to some extent. Considering the reaction (of (72)) immediately after the first cleavage step, there are four products together in the presence of strong acid; azulene, 1-formylazulene, guaiazulene, and 3-formylguaiazulene. 3-Formylguaiazulene will not condense with either of the hydrocarbons, so it irreversibly deformylates to guaiazulene, leaving two pairs of reactants which can condense with each other, i.e. azulene and 1-formylazulene, and guaiazulene and 1-formylazulene. The irreversible deformylation of any 3-formylguaiazulene will increase the concentration of guaiazulene, which in turn

facilitates the speedy removal of 1-formylazulene before it condenses with azulene. The velocity of condensation between 1-formylazulene and guaiazulene might in any case be expected to be higher than that between 1-formylazulene and azulene, because of the greater nucleophilic character associated with the 3- position of guaiazulene compared to the 1(3)- position of azulene.

A similar result is obtained from 3-(3-methylazulen-1--yl)methyleneguaiazulenium perchlorate (91) (CX4). The spectrum (Plate XVI) of the recovered salt shows a hypsochromic shift, with a lowering of intensity ($\log \varepsilon = 4.93$), and a general broadening of the curve. The neutral fraction, containing 18% (w/w) of 1-methylazulene, shows that cleavage at the alternative position, via the intermediate (92), as well as (93), has taken place to a greater extent than at the corresponding one in 3-(azulen-1-yl)methyleneguaiazulenium perchlorate (72). This is as expected, since the additional methyl group renders the two positions for protonation more nearly equal in nucleophilic character.

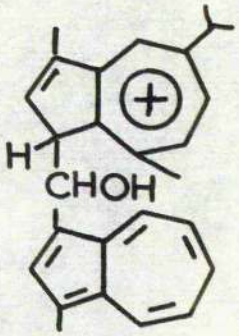
The product from guaiazulene and triphenylmethyl perchlorate (CVIII2), thought to be (94), showed anomalous behaviour in that it did not cleave with boiling HCl (CIX3). This is surprising in view of the previous results, and also because 1-formyl-4-methyl-7-isopropylazulene will not condense with guaiazulene[178], so that the salt might be expected

(94)



(91)

(92)



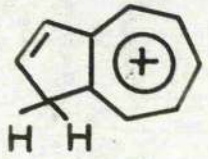
(93)

to cleave completely to give two hydrocarbons. It is noteworthy that the visible absorption maximum (632 mμ.) (see Plate XIX) is also considerably different from the value expected from a comparison with other dye-salts having a comparable degree of alkylation, and it may be that there is another, as yet obscure, electronic factor connected with the stability of the dye-salts, which also affects the course of this reaction.

BIV Azulenium Salts

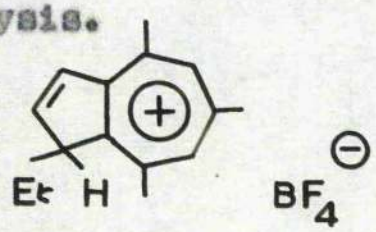
BIV 1 Introduction

For reasons referred to earlier (AVII2), considerable interest attaches to the azulenium salts, of which (95) is the hypothetical parent cation. However, although theoretical considerations[140] have unhesitatingly pointed to the 1(3)- position as the preferred site for protonation when azulenes dissolve reversibly in acid, and a recent study[141] of the proton magnetic resonance spectrum of azulene in carbontetrachloride, and in trifluoracetic acid, has provided experimental confirmation of this, no simple derivatives of the azulenium cation (95) have hitherto been isolated. The

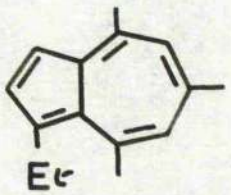


(95)

simplest related compound previously reported[164] in the literature is 1-ethyl-4,6,8-trimethylazulenium fluoroborate (96), which arose from the reaction of 4,6,8-trimethylazulene with triethyloxonium fluoroborate. This colourless salt is stated to yield 1-ethyl-4,6,8-trimethylazulone (97) on hydrolysis.



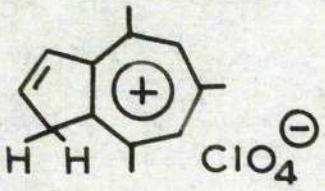
(96)



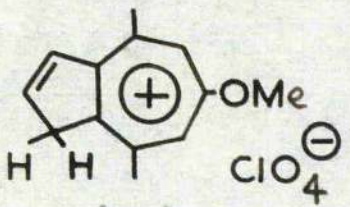
(97)

BIV 2 Isolation and Properties of Azulenium Perchlorates

It has now been found (CVIII1) that 4,6,8-trimethylazulenium perchlorate (98) is precipitated from a solution of the azulene in acetic acid and perchloric acid, by the addition of dry ether, as light brown granular crystals. This salt is fairly stable to the atmosphere when dry, but



(98)



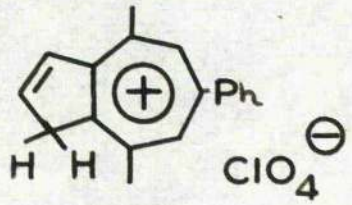
(99)

is hydrolysed at once in the presence of water. In a quantitative hydrolysis experiment (CVII1), 4,6,8-trimethylazulene was recovered in >99% yield, and the perchloric acid was accounted for by volumetric analysis. The perchlorate (98) could not be recrystallised from organic solvents, since it is insoluble in hydrocarbon solvents and ether, while in more polar ones, such as ethanol or acetonitrile, it breaks down to re-form 4,6,8-trimethylazulene and perchloric acid, unless an excess of perchloric acid is present.

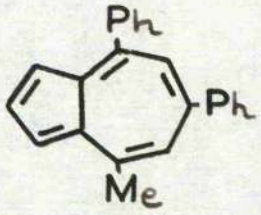
4,8-Dimethyl-6-methoxyazulenium perchlorate (99) was obtained as colourless needles from 4,8-dimethyl-6-methoxyazulene, using an identical procedure (CVII4), and was found to be very similar in properties to (98).

4,8-Dimethyl-6-phenylazulenium perchlorate (100) crystallises directly from a hot solution of the azulene in acetic acid when treated with perchloric acid (CVII3). The

product obtained in this way is in the form of dark green needles, and gives satisfactory analytical data, but if the procedure for the previous two salts is used, with an excess of perchloric acid, pale yellow needles are obtained. The green colour is presumably due to the presence of traces of 4,8-dimethyl-6-phenylazulene. This salt may be recrystallised from acetonitrile (green needles).

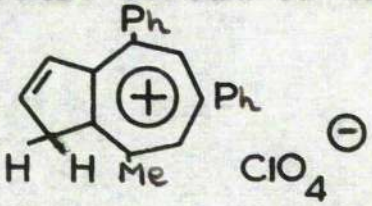


(100)

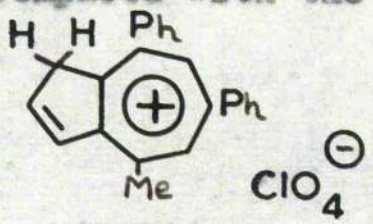


(77)

When 4,6-diphenyl-8-methylazulene (77) was treated in the same way (CVII2), some salt was obtained as green needles by the addition of ether, but it could not be isolated in a pure condition, and no satisfactory analysis was obtained. (C.f. Behaviour of this azulene with ethyl orthoformate and perchloric acid, (CV8)). It seems likely that protonation takes place to a comparable extent at both 1- and 3- positions to give a mixture of salts (101) and (102). The difference in electronic effect of the 4-phenyl compared with the



(101)

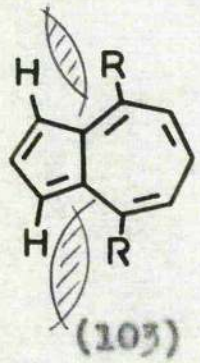


(102)

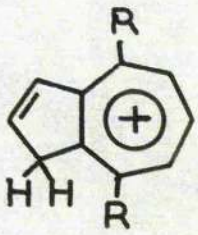
4-methyl substituent must account for the relative instability of this product.

It is significant that the only azulenium salts which have been successfully isolated so far carry methyl substituents in the 4- and 8- positions. This may be a necessary condition.

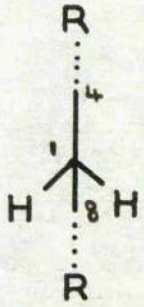
If scale models of the appropriate molecules are considered, it may be seen that there is a greater degree of steric interaction between the 1(3)-hydrogen atoms and a 4(8)- substituent in a 4,8-disubstituted azulene (e.g. (103)) than in its conjugate acid (104a).



(103)



(104a)



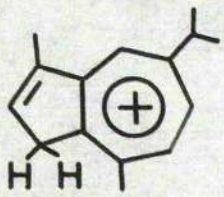
Projection of 4,8-disubstituted-azulenium cation viewed along $C_{(2)} - C_{(6)}$ axis

(104b)

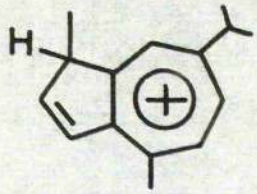
Although the azulene nucleus in (103) may be preferred to the vinyltropylium structure (104) by virtue of the resonance stabilisation attending it, there is nevertheless a compressional energy barrier to be overcome, against change of carbon atom$_{(1)}$ from the Sp^3 state in (104) to the Sp^2 state in the azulene (103), and this may hinder deprotonation sufficiently to allow isolation of the salt.

It is evident that this naive view does not express the whole truth, for, arguing on these lines, it is curious

that no salt has been isolated from guaiazulene. Since 1,3-dimethylazulene is soluble in strong acid, it is probable that guaiazulene forms two cations in equilibrium, (105) and (106), when dissolved in acid. Only (105) would suffer the steric hindrance to deprotonation referred to



(105)



(106)

above. It is unlikely, however, that (106) would predominate in the equilibrium since there will be steric hindrance to protonation of guaiazulene at this position. The necessary conditions for the isolation of an azulenium salt may perhaps be related to the stabilisation of the cation by electron release of the alkyl groups and unresolved differences of fine structure in this respect.

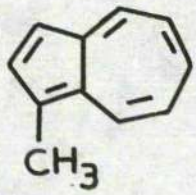
Shortly after our preliminary publication[195] appeared, reporting the isolation of 4,6,8-trimethylazulenium perchlorate, it was reported[196], without experimental details or the mention of any specific compound, that "azulene and its alkylated derivatives" give azulenium salts as colourless crystals on treatment with 54% HBF_4 in ether.

BV 1(3)-Methylazulenes

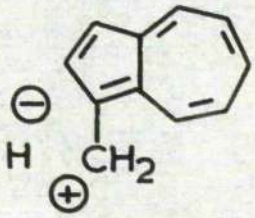
BV 1 Introduction

As the concept of azulene (1) as a readily polarisable molecule, with polar resonance structures such as (1b) making important contributions to the ground state developed, it became clear that there is a high degree of electronic interaction between substituents and the electrons of the nucleus. Structures where multiple bonds are attached to, and conjugated with, the nucleus at $C_{(1)}$, or $C_{(3)}$, show especially abnormal properties (C.f. BII).

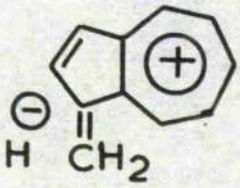
Consideration of these facts made it apparent that considerable interest would attach to the properties of the 1(3)-methylazulenes, for it is possible that a 1(3)-methyl group interacts to a significant extent by hydride hyperconjugation. On such an hypothesis, polar structures such as (107b) and (107c) would make significant contributions to the ground state of 1-methylazulene (107a).



(107a)



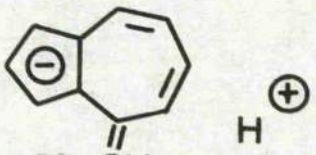
(107b)



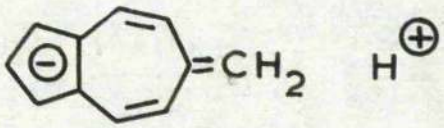
(107c)

Hyperconjugation in which a canonical structure with a non-bonded proton is obtained by electron release by a carbon-hydrogen bond, is a familiar and useful concept[197]. A recent example of its use in the alkylated benzene series

was to explain the relative rates of hydrolysis of m-alkylbenzhydryl chlorides, where enhancement of the reaction rate was found to follow the order methyl > ethyl > isopropyl > tert. butyl. This observation was rationalised by assuming cationic hyperconjugation from the m- position[198]. The concept has also been used to interpret spectral displacements brought about by the alkylation of non-alternant hydrocarbons. The fact, for instance, that the bathochromic component of the displacement of visible absorption frequencies for 4- and 6- alkylated azulenes is greater than that expected by calculation from an L.C.A.O.-M.O. model, can be attributed to the probability that the 4- and 6- positions are the ones which most favour hyperconjugation. This is because the polarisability of the nucleus stabilises the hyperconjugative forms, giving rise, for instance, to structures of type (108) and (109)[199].



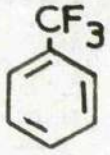
(108)



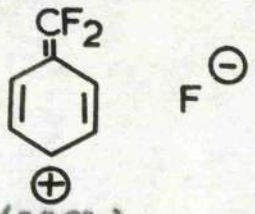
(109)

It appears, however, that hydride hyperconjugation, in which the hydrogen atom accepts the bonding electrons, may also be of importance. It is known[200,201] in the alcohol series that the acidities follow the order methyl > ethyl > n-propyl > isopropyl > secondary butyl > tert. butyl; a fact which is demonstrated by the marked decrease in reactivity

towards sodium which is found in progressing along this series. Solvation or inductive effects have been shown[202] to be unable to account for this, and the effect of steric strain would be expected to produce the reverse order of acidity if it was effective. It was suggested[201] that the observed order results from hydride hyperconjugative stabilisation of the alkoxide ions, through the α-hydrogen atoms. Replacement of α-hydrogen atoms by alkyl groups thus reduces the number of such canonical forms possible. It was subsequently shown[202] that the C-H stretching frequencies showed appropriate shifts between pairs of alcohols and alkoxide ions. This kind of hyperconjugation is analogous to that proposed by Roberts[203] to explain the directive effect of the trifluoromethyl group in aromatic substitution. He suggested that structure (110b) makes an important contribution to trifluoromethylbenzene (110a).



(110a)



(110b)

Experimental results, which are discussed in the following sub-sections, have broadly substantiated this idea with respect to 1(3)-methylazulenes.

BV 2 Infra-Red Spectra of 1(3)-Methylazulenes

The assumption that resonance forms such as (107b) contribute to 1-methylazulene implies a weakening, with

consequent lowering of the stretching frequency, of the C-H bonds. Some relevant infra-red spectral data is shown in Table 19. Only one systematic study of the infra-red spectra of azulene and alkylated azulenes is recorded[204] in the literature, and here the exact values for ν_{CH} (stretching) are not stated, although the general shape of the absorption curves reproduced in the paper agree with the present findings (see e.g. Plate XXI).

Among the compounds considered in Table 19, with the exception of guaiazulene, there are only two types of C-H bond present, viz., those in the methyl groups, and those in the aromatic rings. The only mode of vibration with frequencies in this range is the C-H (stretching)[205]. It seems reasonable to assign the group of absorption frequencies above 3000cm.$^{-1}$ to the aromatic -CH= group, and those below to the alkyl groups. This is confirmed by a comparison of the curves for 1-methylazulene, and 1,3-dimethylazulene (Plate XXI), where it can be seen that practically the only difference is that in the one for 1,3-dimethylazulene, the relative intensity of the lower to the higher frequency range is greater. For comparison, the highest recorded absorption maxima (peaks A and B, Table 19) are selected.

The only valid comparison which can be made to test the hypothesis of hydride hyperconjugation is between 1-methylnaphthalene and 1-methyl and 1,3-dimethylazulene.

Compound	Frequencies of Absorption Maxima recorded in range 2703-4000 cm.$^{-1}$ (in CCl_4) (cm.$^{-1}$)	Principle Peaks A	B
4,6,8-Trimethylazulene	3110, 3080, 2985, 2953, 2927, 2859.	3080	2927
1-Methylnaphthalene	3071, 2965, 2932, 2860, 2736	3071	2932
1-Methylazulene	3027, 2973, 2919, 2863, 2740	3027	2919
1,3-Dimethylazulene	3027, 2965, 2917, 2861, 2737	3027	2917
Guaiazulene	3071, 2962, 2927, 2867	3071	2962

Table 19 Infra-Red C-H stretching frequencies of some alkylazulenes and 1-methylnaphthalene.

Note: Principle peak A:- Highest maximum recorded 3000 cm.$^{-1}$

" " B:- Highest maximum recorded 3000 cm.$^{-1}$

Guaiazulene, with its three alkyl groups in different positions is too complex to inspire confidence in a correct interpretation, and the spectrum of 4,6,8-trimethylazulene must be viewed with some caution since it is to be expected that the 4- and 6-methyl groups may show a comparable lowering of the C-H stretching frequency by cationic hyperconjugation (C.f. (108) and (109)).

Considering these three compounds suggested, it is seen that the methyl group C-H stretching frequency (Peak B Table 19) of 1-methyl and 1,3-dimethylazulene is less than that of 1-methylnaphthalene by 13 and 15 $cm.^{-1}$ respectively, as expected. At the wavelength of 3.5μ, the accuracy of determination is probably $\pm$ 0.005μ, which gives an error of $\pm$ 4 $cm.^{-1}$ in the frequency. The error in the difference can therefore be up to 8 cm^{-1}, so the differences observed (13 and 15 cm^{-1}), although small, are real. Considered in isolation, this would not seem very convincing, but in the light of chemical data discussed later (BV 3, BV 4, BV 5), it serves as confirmatory evidence.

It should be noted that the differences ($\Delta\nu_{CH}$) observed here are much less than those found between alcohols and their alkoxide ions (of the order of 200 $cm.^{-1}$)[202], but again it must be emphasised that it is the polarisability of azulene, rather than its polarisation, which is significant. In the sodium alkoxides, the negatively charged oxygen atom constitutes a strong driving force in the direction of anionic hyperconjugation.

A study of the proton magnetic resonance spectrum of these compounds would be of interest, for the methyl group protons of 1(3)-methylazulenes would be expected to show increased electronic shielding. An important advantage of using this technique would be that it should show the direction

of polarisation, for infra-red data cannot distinguish between the two possibilities of anionic and cationic hyperconjugation.

BV 3 Reaction of Azulenes with Triarylmethyl Perchlorates:

Introduction

Triphenylmethyl perchlorate has recently been developed[206] as a useful reagent for the dehydrogenation of hydroaromatic compounds. It functions in a way which is analogous to that proposed[207] for dehydrogenation by quinones, that is, by successive removal of a hydride ion and a proton, as shown in Fig. 10.

$$Ph_3C^+ + R_3CH \underset{\text{Step I}}{\rightleftharpoons} R_3C^+ + Ph_3CH$$

$$R_3C^+ \xrightarrow[\text{Step II}]{} \text{Neutral Product} + H^+$$

Fig. 10 Dehydrogenation by Triarylmethyl Salts.

This process occurs in two discrete steps, and, if the intermediate cation R_3C^+ is sufficiently stable, it may be capable of isolation as its salt. Such a case is the formation of tropylium salts from cycloheptatriene[208,209].

Whether the second step, of loss of a proton from the cation R_3C^+, will take place will depend on its acidity, which is determined by the relative stabilities of R_3C^+ and its conjugate base.

In the 1(3)-methylazulene series, if the theories outlined in (BV 1) are appropriate, the obvious site for loss of

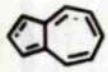
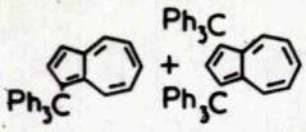
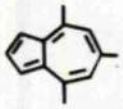
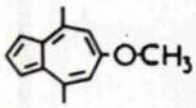
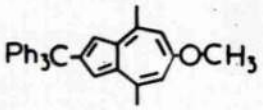
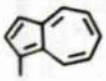
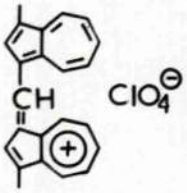
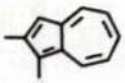
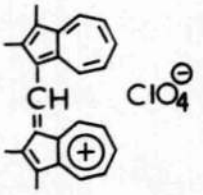
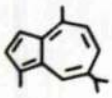
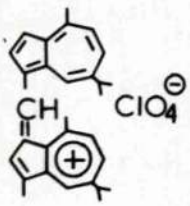
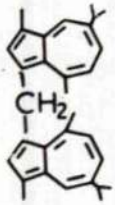
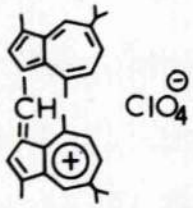
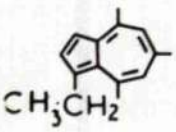
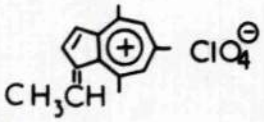
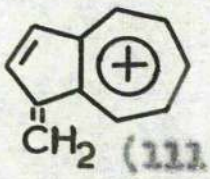
Azulene.	Product.	Reference.
		192
	No reaction	192
	 (?) (A)	C,VIII,10
		C,VIII,1
	 (?)	C,VIII,8
		C,VIII,2
		192
	 (?)	C,VIII,9

Table 20. Products of reaction of azulenes with triphenylmethyl perchlorate.

hydride ion in the initial step (Fig. 10) is the 1(3)-methyl group(s). The 1(3)-methyleneazulenium cation thus produced (e.g. (111)) is reactive. It cannot be stabilised by loss of a proton, but undergoes nucleophilic attack by a molecule of the azulene. The overall result is an intermolecular dehydrogenation involving 3 hydrogen atoms. A summary of the products encountered in reactions of triphenylmethyl perchlorate with azulenes is given in Table 20, and each case is discussed individually in the ensuing text.



(111)

BV 4 Substitution of Azulenes by the Triphenylmethyl Cation

Azulene, boiled with a solution of triphenylmethyl perchlorate in acetic acid, gave a mixture of 1-triphenylmethylazulene, and 1,3-bistriphenylmethylazulene; the bis-substitution product was the more readily formed[192]. No reaction took place with 4,6,8-trimethylazulene under the same conditions[192], evidently because the 4- and 8-methyl substituents effectively screen the 1- and 3- positions of the nucleus against electrophilic attack by the bulky triphenylmethyl cation. Replacement of the 6-methyl group by a 6-methoxy group, however, induces reaction (CVIII 10), and results in a high melting, ruby-red, and beautifully crystalline product (Product A, Table 20). Unfortunately, insufficient material was available for a complete characterisation.

Table 21 shows the visible absorption maxima of product A and some related compounds. For the reaction of 4,8-dimethyl-6-methoxyazulene with triphenylmethyl perchlorate

Azulene	λ max. (mμ)	Log ε	Ref.
4,8-Dimethyl-6-methoxyazulene	515	2.56	DVII
Product A	505	2.61(a)	CVIII 10
Azulene	580(b)	2.54	-
1-Triphenylmethylazulene	602	2.49	192
1,3-Bistriphenylmethylazulene	622	2.54	192

Table 21 Visible absorption maxima of Product A (see Table 20) and related azulenes in benzene (see Plates XVII and XVIII).

Note: (a) Calculated on the basis of its being a mono-(triphenylmethyl) derivative of 4,8-dimethyl--6-methoxyazulene.

(b) The visible spectrum of azulene shows fine structure; this is the absolute maximum in the visible region.

(CVIII 10), two molecular proportions of the perchlorate were used, in order to favour the di-substitution product, should it be formed, rather than a mixture of the mono- and di--substitution products.

Table 21, however, shows that there is no correlation of the absorption maximum position of product A with those expected for 1-triphenylmethyl-4,8-dimethyl-6-methoxyazulene

or 1,3-bistriphenylmethyl-4,8-dimethyl-6-methoxyazulene (537 m.μ. or 557 m.μ. respectively) by comparison with azulene, 1-triphenylmethylazulene and 1,3-bistriphenylmethylazulene. It must be borne in mind, however, that the effects of steric interaction in such molecules might cause divergence from such simple additivity rules. With lack of sufficient data for a definite decision, these must remain tentative possibilities.

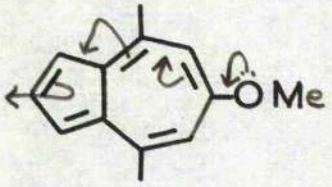
The fact, however, that the spectral shift of product A relative to the parent 4,8-dimethyl-6-methoxyazulene is hypsochromic (C.f. azulene and 1-triphenylmethylazulene), suggests that a different position of substitution may be involved. Two other positions are vacant, viz., the 2- and the 5(7)- positions. According to the Plattner rules[8], the average wavelength displacements associated with alkylation of the 2- and 5(7)- positions are -20 m.μ. and +15 m.μ. respectively. Position 2- thus appears more likely to be involved, and it is also the one to be expected on grounds of steric freedom.

According to theoretical calculations[63], the electron densities at the 2- and 5(7)- positions are about the same. A slight difference either way may be obtained, depending on which model the calculations are based on. The atom localisation energy of the 5(7)-position has been calculated[132] as 2.341 β units, compared with 2.362 β units

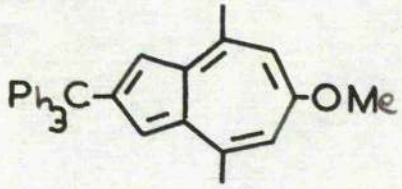
for the 2- position, but again, this difference is slight when compared to the 1.924 β units for the 1(3)- position. Naturally, considerable caution must be exercised in applying these conclusions, reached for azulene, to the substituted molecule 4,8-dimethyl-6-methoxyazulene, but at least they indicate that there is no gross effect inherent in the structure of the nucleus which would favour electrophilic substitution at the 5(7)- position, rather than the 2- position, when the 5(7)- position is subject to steric screening to as much as, or a greater extent than, the much more reactive 1(3) position. Apart from this, the effect of the 6-methoxy group would be expected to favour the 5(7) position.

1-Triphenylmethylazulene and 1,3-bistriphenylmethylazulene are the only azulenes known with triphenylmethyl substituents, so not many conclusions can be drawn about their effect on the visible absorption spectrum. However, successive substitution of azulene in the 1- and 3- positions by the triphenylmethyl group causes progressive bathochromic displacements of λmax. of 22 and 20 m.μ. respectively, whereas the average displacement associated with an alkyl group in these positions is +36 m.μ. Therefore, since alkylation of the 2- position of azulene causes a shift of -20 m.μ.[8], the observed shift of -10 m.μ. for product A relative to (112) is in good agreement with the hypothesis that it is 2-triphenylmethyl-4,8-dimethyl-6-

-methoxyazulene (113).



(112)



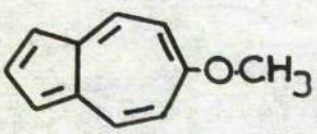
(113)

The positions of the infra-red absorption peaks for the same series of compounds in the 5-10 μ region, shown in Table 22, provide inconclusive evidence. The only conclusion which may be drawn is the negative one that there are no strong resemblances between the relation of the absorption pattern of 4,8-dimethyl-6-methoxyazulene to that of product A, and that of azulene to that of its 1(3)-substituted derivatives.

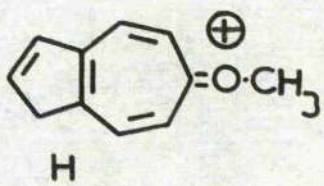
A point of interest which emerges from Table 22, is the absorption peak at 1333 and 1337 cm^{-1}, shown by 4,8-dimethyl--6-methoxyazulene and product A respectively. This is probably the C-O stretching frequency associated with the 6-methoxy group. If so, it is somewhat higher than the normal range[205] (1230-1270) expected for aryl and aryl-alkyl ethers. Electron release by this substituent will endow the C-O link with some double bond character, and on this assumption, canonical forms such as (114 b, c and d) must contribute significantly to the structure of the 6-methoxy-azulene (114a).

Azulene	1-Triphenylmethylazulene	1,3-bis-triphenylmethylazulene	4,8-Dimethyl-6-methoxyazulene	Product A	Triphenylmethane
1575	1585	1587	1577	1577	1595
1529	1563	1563	1333	1484	1490
1290	1302	1403	1209	1337	1460
1200	1215	1290	1188	1258	1312
1147	1189	1176	1171	1217	1245
1050	1176	1151	1100	1182	1153
1010	1153	1074	1070	1175	1076
	1076	1030	1016	1106	1029
	1032			1156	1002
				1153	
				1087	
				1067	
				1033	
				1001	

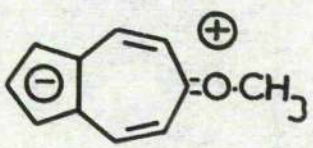
Table 22 Frequencies of I.R. absorption maxima ($cm.^{-1}$), in the range 2000 - 1000 $cm.^{-1}$, for Product A (see Table 20), and some related compounds (in Nujol).



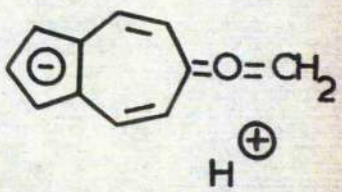
(114a)



(114b)



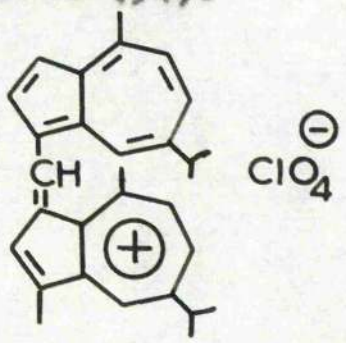
(114c)



(114d)

BV 5 Reaction of 1(3)-Substituted Azulenes with Triarylmethyl Perchlorates

The reaction of triphenylmethyl perchlorate with an excess (400%) of guaiazulene (CVIII2) gave a dye-salt in 45% yield, considered to be 3-(4-methyl-7-isopropylazulen-1-yl)-methyleneguaiazulenium perchlorate (94).



(94)

In a consideration of its structure, there are three important points to consider.

(i) Its spectrum (see Plate XIX) closely resembles that of other dye-salts whose structure is now established beyond doubt. This fact, and its resemblance in other properties to these dye-salts clearly shows it to be a substituted 1,1'-azulenylmethyleneazulenium perchlorate.

(ii) Triphenylmethane was isolated from the mother liquor (CVIII2), demonstrating that hydride ion abstraction had taken place.

(iii)An identical dye-salt is obtained when the triphenylmethyl cation used has electron releasing p- substituents. Thus tri-p-chlorophenylmethyl, p-methoxyphenyldiphenylmethyl, and tri-p-methoxyphenylmethyl perchlorates all gave a product (CVIII) which was identical with that from

guaiazulene and triphenylmethyl perchlorate (CVIII2), on the basis of analytical data and comparisons of the visible spectra. This shows that the phenyl groups of the triarylmethyl cation form no part of the resultant structure. The observation is also interesting in that it demonstrates the considerable affinity for hydride ion of the triphenylmethyl cation. Reaction still occurs even when the positive charge is attenuated by electron releasing p-substituents. Only in the case of tri-p-methoxyphenylmethyl perchlorate were slightly more vigorous conditions required for the reaction (boiling under reflux for 35 mins. (CVIII7)).

To interpret this data, the scheme outlined in Fig. 11 is suggested. The first stage, that of hydride ion abstraction, has been clearly established by the foregoing evidence, and any site other than the 3-methyl group could not ultimately yield a 1,1'-azulenylmethyleneazulenium salt. After this, however, certain difficulties arise. It is necessary to explain the elimination of a molecule of hydrogen from the intermediate (115). This may occur through a further dehydrogenation reaction with triphenylmethyl perchlorate, leading to intermediate (116), for the yield did not exceed 50% based on triphenylmethyl perchlorate. The reaction of 1-methylazulene with triphenylmethyl perchlorate, however, gives a yield of the dye-salt as high as 82% (CVIII1), although the two reactions are not strictly

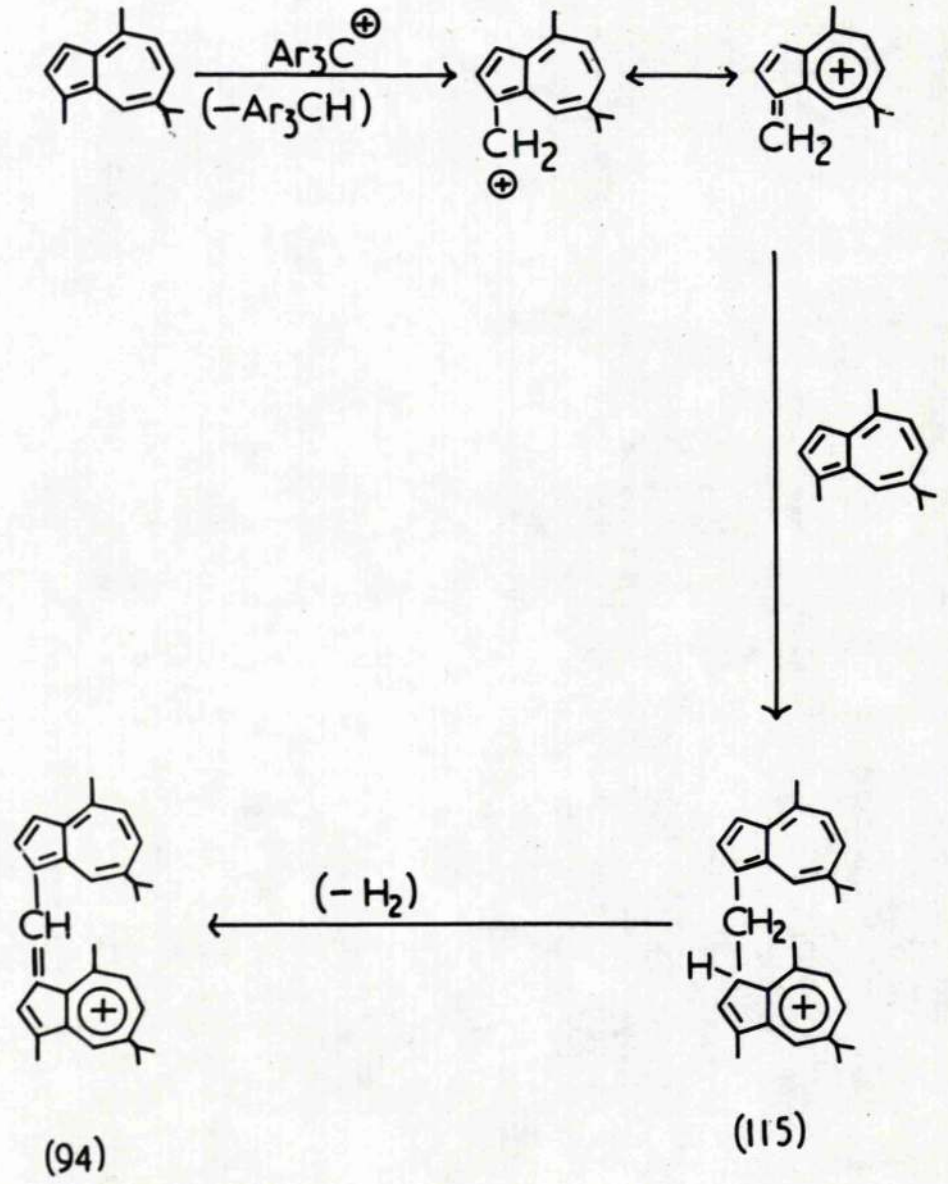
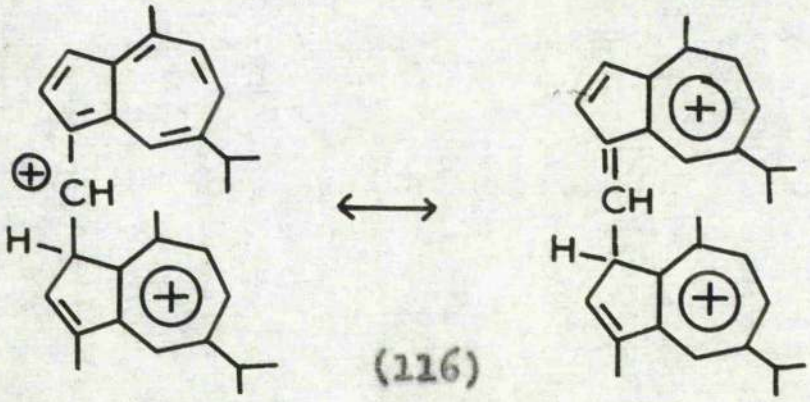


Fig.11. Reaction of guaiazulene with triarylmethyl perchlorates.

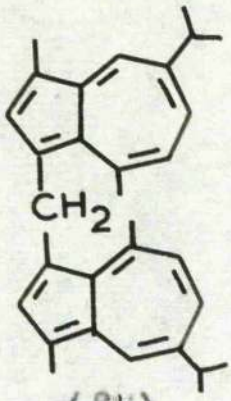
comparable since different types of product result (see below). The elimination of a molecule of hydrogen from



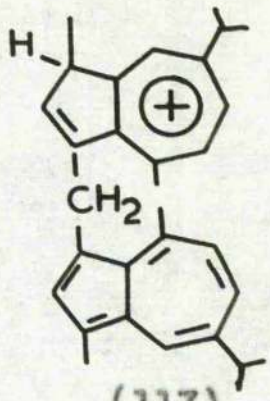
(116)

(115) may on the other hand be a purely thermal process, and be promoted by what must undoubtedly be a considerable increase in resonance stabilisation attending the formation of the 1,1'-azulenylmethyleneazulenium structure (94).

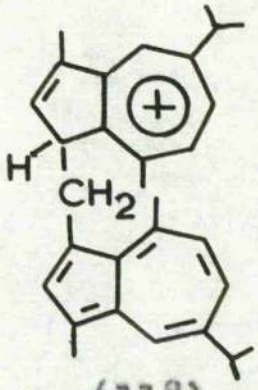
A serious objection to the latter view emerges from evidence[178] concerning the behaviour of 3,3'-diguaiazulenylmethane (84) when boiled with strong acid. This methane (84), although sufficiently basic to dissolve, is recovered unchanged. It is to be expected that, in acid solution, protonation will occur at all four 1(3)- positions, so that there will be an equilibrium between the two structures (117) and (118). This latter (118), however, is the same type of structure as the intermediate (115) postulated in the reaction leading to dye-salt (94) (Fig. 11), and it would therefore be expected to undergo irreversible dehydrogenation to the dye-salt (21) when boiled with perchloric acid. Dehydrogenation of the methane (84) to the dye-salt (21) can only be effected by triphenylmethyl



(84)



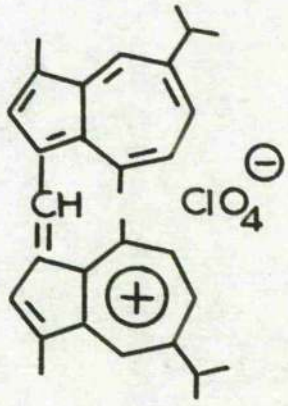
(117)



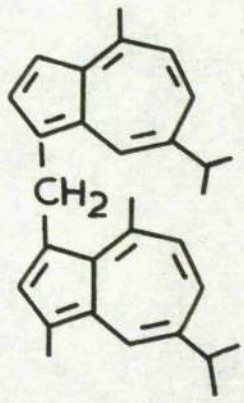
(118)

perchlorate[27].

To complete the investigation satisfactorily it would be necessary to sythesise the methane (119) and the dye-salt (94) independently.

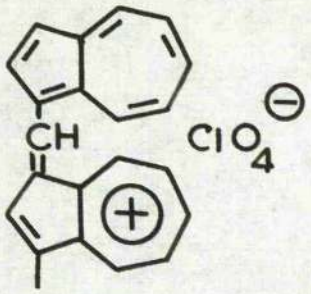


(21)

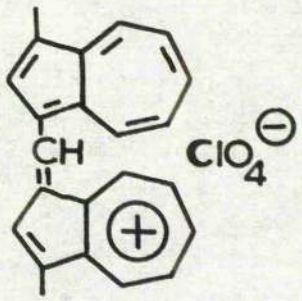


(119)

1-Methylazulene reacts in a more complicated manner with an excess of triphenylmethyl perchlorate (CVIII1), yielding 1-(3-methylazulen-1-yl)methylene-3-methylazulenium perchlorate (73). By analogy with the reaction of guaiazulene it would be expected to give 1-(3-methylazulen-1--yl)methyleneazulenium perchlorate (71). Both salts, (71) and (73), have been synthesised independantly (CII2, CV2). The visible spectra (Plates XIII, XX), infra-red spectra, and X-ray powder diagrams for the two salts (71) and (73) and the product of the reaction of 1-methylazulene with



(71)



(73)

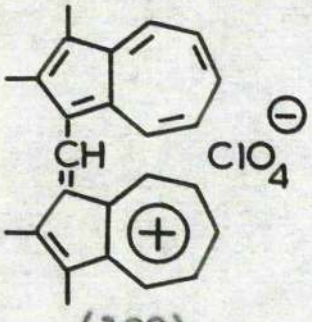
triphenylmethyl perchlorate were compared, and the comparisons clearly established (73) as the structure of the latter.

On working up the mother liquor from this reaction (CVIII1), triphenylmethane was again isolated in high yield, and the remaining azulenic material was analysed by gas-liquid chromatography, which showed it to consist of 1-methylazulene and azulene in the ratio 8·5:1 (w/w). In this experiment (CVIII1), a mixture of 1-methylazulene (0.00251 moles) and triphenylmethyl perchlorate (0.000495 moles) reacted to give the dye-salt (73) (0.000403 moles). The azulene mixture after reaction would therefore be expected to consist of 1-methylazulene (0.0013 moles) and azulene (0.000403 moles), which is equivalent to a (w/w) ratio of 3·6:1. The quantitative aspect of this experiment is therefore far from satisfactory, but nevertheless it is useful in qualitatively demonstrating the presence of azulene, which is an expected consequence of the dye-salt possessing structure (73).

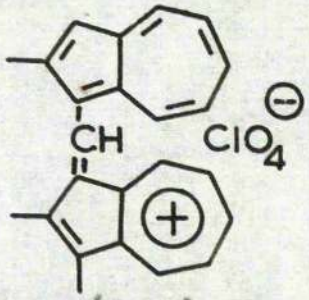
It was found (see BIII 6) that 1-methylazulene will displace azulene from the dye-salt (71) when the two componants are boiled together in acetic acid, but it is unlikely that

this simple reaction will account for the behaviour of 1-methylazulene with triphenylmethyl perchlorate for two reasons. (i) The displacement reaction does not go to completion. None of the experiments conducted (CX) gave more than a 50% displacement of azulene by 1-methylazulene. (ii) The reaction of 1-methylazulene with triphenylmethyl perchlorate (CVIII1) appears to still be essentially the same when the triphenylmethyl perchlorate is kept in excess throughout the reaction. In this case the product is much less pure, and may or may not contain 1-(3-methylazulen-1-yl)-methyleneazulenium perchlorate (71), among other contaminants, but it still has a sharp absorption maximum at 651 mμ. (Plate XX).

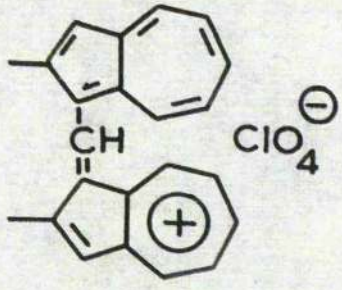
1,2-Dimethylazulene reacted with triphenylmethyl perchlorate to give 1-(2,3-dimethylazulen-1-yl)methylene-2,3--dimethylazulenium perchlorate (120) (CVIII8). The evidence for this rests on the visible spectrum of the product.



(120)



(121)



(122)

Unfortunately, neither this product nor the related compounds (121), and (122), required for comparison, could be obtained in sufficient quantity to purify them for analysis. There

was insufficient 1,2-dimethylazulene to repeat the work and it is only available through a long and tedious synthesis (DIII and DIV). However, by making the reasonable assumption (C.f. BIII 5) that the spectral shifts due to alkylation are more or less additive for this group of 1-(2-methylazulen-1--yl)methylene-2-methylazulenium salts ((120), (121) and (122)), structure (120) can be safely assigned to this product. The salts (121) and (122) were synthesised unambiguously (CII 4, CII 5), although they were not isolated in sufficient quantity for analysis, and showed absorption maxima (acetic acid) at 655 and 641 m.μ. respectively.

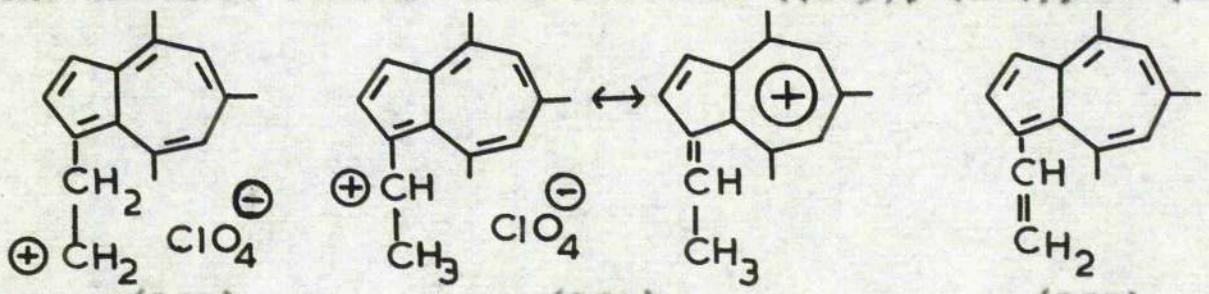
The product from 1,2-dimethylazulene and triphenylmethyl perchlorate showed an absorption maximum (acetic acid) at 667 mμ. Thus the difference between λmax. for this product and (121) is 12 mμ., and between (121) and (122) it is 14 mμ. This is in good agreement with the product having structure (120). (At the time this experiment was carried out, no gas-chromatography equipment was available for analysing the mother liquor).

Following these experiments, it was of evident interest to investigate the action of triphenylmethyl perchlorate on higher 1(3)-alkylated azulenes, since the 1(3)- (substituted methylene) azulenium salts resulting from hydride ion abstraction from the α-position are comparitively stable. 3,3'-Diguaiazulenylmethane (84) yields, as expected, the dye-

-salt (21),[192] which is identical with the products of condensation of guaiazulene with α-oxoaldehydes in the presence of perchloric acid. A 1-ethylazulene should afford a 1-ethylideneazulenium perchlorate, and members of this series are independently accessible through condensations of azulenes with acetaldehyde and perchloric acid (CI26 and CI27). 4,6,8-Trimethylazulene was selected, since the 1-ethyl derivative is known and characterised[164]. The reported preparation involved the reaction of 4,6,8-trimethylazulene with ethyloxonium fluoroborate. For the present work, the more convenient procedure of reducing 1-ethylidene-4,6,8-trimethylazulenium perchlorate with lithium aluminium hydride was adopted (DIX). On treating 1-ethyl-4,6,8-trimethylazulene with triphenylmethyl perchlorate (CVIII 9), the reaction mixture turned from blue to the expected yellow, but the solid material which was isolated was very unstable, presumably owing to contamination with triphenylmethyl perchlorate. 1-Ethylidene-4,6,8-trimethylazulenium perchlorate is itself too unstable to allow of purification by washing with aqueous solvents, or recrystallisation.

Although not entirely satisfactory, this experiment does prove that no formation of a dye-salt takes place in this case. Hydride ion abstraction was shown to occur by the isolation of triphenylmethane. The product could possess

one of three reasonable structures ((123), (124), or (125)).



(123) (124) (125)

Structure (125) would be ether soluble, and of the remaining two possibilities, (124) is clearly the most likely, both from theoretical considerations, and from the observed colour.

To summarise the findings of these latter sub-sections, azulenes in which the 1- and 3- positions are unsubstituted and sterically unhindered, undergo normal electrophilic substitution by triphenylmethyl perchlorate. Azulenes with a substituted or unsubstituted methyl group in the 1(3)-position suffer hydride ion abstraction from the α-carbon atom to form 1(3)- (substituted methylene)azulenium salts. 1(3)-(Unsubstituted methylene)azulenium salts cannot be isolated and undergo further interaction with the azulene to form a 1,1'-azulenylmethyleneazulenium salt, by a mechanism which has not been elucidated.

Introductory Notes

Melting points were determined on a Kofler-type heating stage.

Visible spectra were measured with a Unicam S.P. 600 instrument. Absorption data for the majority of new compounds are recorded immediately after the analytical results. The wavelengths of absorption maxima are given in m.μ., followed (in parentheses) by intensities of absorption in $\log_{10}\varepsilon$ units.

Infra-red spectra were recorded with a Grubb-Parsons Type G.S.2A. instrument.

The specifications for analyses of azulene mixtures by gas-liquid chromatography are given in the Appendix.

Micro-analyses were performed by Drs. Weiler and Strauss, Oxford. Unless otherwise stated, samples of perchlorates were dried for 6-8 hours at $80^{\circ}/0.1$ m.m. before analysis, and those of other compounds usually 5-6 hours under the same conditions. Samples dried in vacuo, were over potassium hydroxide and phosphoric anhydride.

Chromatography was on activated alumina.

Materials: Azulene and guaiazulene were commercial products (Rütgerswerke-Aktengesellschaft, Fluka A.G., and L. Light & Co. Ltd.), and were purified where necessary by chromatography and/or distillation at reduced pressure immediately before use.

Other starting materials, for which preparative details are not mentioned in sections C or D, were purchased, and purified, where necessary, by distillation or recrystallisation, as appropriate.

Perchloric acid refers to 70-72% (w/w), AnalaR grade, unless otherwise stated. Hydrogen bromide in acetic acid refers to a 50% (w/w) solution. Glyoxal refers to a 30% (w/w) aqueous solution.

Solvents: Acetic acid, and the benzene used for spectral work, were of AnalaR grade.

Acetonitrile was purified by boiling for 30 minutes with phosphoric anhydride, then distilled, and was redistilled before use.

Tetrahydrofuran was boiled over sodium wire until it no longer discoloured the fresh metal surface, and was then distilled from sodium immediately before use.

Ethanol was dried with sodium and diethylphthalate, as described by Vogel[231], and methanol was dried by boiling with magnesium turnings and then distilling, as described by Weissberger[232].

Ether and petroleum-ether were purified where necessary by allowing them to stand for several days over sodium wire, and then distilling them. Light petrol refers to petroleum--ether (b.pt. 40-60°), and petrol to petroleum-ether (b.pt. 60-80°).

The proportions of solvent mixtures are expressed as volume:volume ratios unless otherwise stated.

CI Condensation of Azulenes with Carbocyclic and Heterocyclic Aromatic, and Aliphatic, Aldehydes in the Presence of Perchloric Acid

CI 1 Guaiazulene with Benzaldehyde

A solution of guaiazulene (400 mgs.) and benzaldehyde (200 mgs.) in tetrahydrofuran (10 ml.) was treated with perchloric acid (0.5 ml.) at room temperature. The reddish-brown solution began to deposit crystals at once. After the mixture had been allowed to stand for one hour, 3-benzylideneguaiazulenium perchlorate (578 mgs., 75%) was filtered, washed with tetrahydrofuran followed by ether, and dried in vacuo. Recrystallisation from acetic acid gave orange needles, m.p. 195-200°(d).

Found; C 68.2 H 6.1 Cl 9.7,

$C_{12}H_{23}ClO_4$ requires 68.3 6.0 9.2%

λmax. (acetic acid) 456 (4.09)

CI 2 Guaiazulene with 3-Formylpyrene

Guaiazulene (200 mgs.) and 3-formylpyrene (230 mgs.), allowed to react under the same conditions as for experiment (CI 1) above, yielded 3-(3-pyrenyl)methyleneguaiazulenium perchlorate as dark green needles (430 mgs., 85%), which,

after recrystallisation from acetic acid, decomposed $>230^{\circ}$.

Found; C 75.2 H 5.5 Cl 6.9,

$C_{32}H_{27}O_4Cl$ requires 75.2 5.3 6.9%

λ max. (acetic acid) 597 (4.41).

CI 3 Guaiazulene with 1-Formylnaphthalene

A solution of guaiazulene (400 mgs.), 1-formylnaphthalene (0.35 ml.), and perchloric acid (1 ml.) in acetic acid (10 ml.) was boiled for 2 minutes, and then allowed to cool, and stand at room temperature for two days. 3-(1-Naphthyl)-methyleneguaiazulenium perchlorate (33%) was obtained as red needles, which were recrystallised from acetic acid, m.p. 195--220°(d).

Found; C 71.1 H 5.6 Cl 8.6,

$C_{26}H_{25}ClO_4$ requires 71.5 5.8 8.1%

λ max. (acetic acid) 503 (4.30).

CI 4 Guaiazulene with o-Hydroxybenzaldehyde

A mixture of guaiazulene (600 mgs.), o-hydroxybenzaldehyde (370 mgs.), perchloric acid (1 ml.), and tetrahydrofuran (10 ml.) was heated to the boiling point and then allowed to cool to room temperature. 3-o-Hydroxybenzylideneguaiazulenium perchlorate (57%) was filtered off as reddish-brown needles, m.p. 220-225°(d). This product was analysed without recrystallisation.

Found; C 65.1 H 6.0 Cl 8.9,

$C_{22}H_{23}ClO_5$ requires 65.6 5.8 8.8%

λ max. (acetic acid) 499 (4.28).

CI 5 Guaiazulene with p-Hydroxybenzaldehyde

A mixture of guaiazulene (600 mgs.), p-hydroxybenzaldehyde (370 mgs.), perchloric acid (1 ml.) and tetrahydrofuran (10 ml.) was treated in the same way as in experiment CI 4 above. 3-p-Hydroxybenzylideneguaiazulenium perchlorate was obtained as brown needles which decomposed $> 230^{\circ}$. The product was analysed without recrystallisation.

Found; C 65.5 H 5.9 Cl 8.9,

$C_{22}H_{23}ClO_5$ requires 65.6 5.8 8.8%

λ max. 523 (4.51).

CI 6 Guaiazulene with p-Methoxybenzaldehyde

A mixture of guaiazulene (2 gms.), p-methoxybenzaldehyde (1.36 gms.), perchloric acid (1 ml.) and acetic acid (5 ml.) was boiled for one minute, then cooled and filtered, yielding 3-p-methoxybenzylideneguaiazulenium perchlorate (36%) as reddish-brown needles. After recrystallisation from acetonitrile the m.p. was 201-203°.

Found; C 66.6 H 6.2 Cl 8.2,

$C_{23}H_{25}ClO_5$ requires 66.3 6.1 8.5%

λ max. (acetic acid) 515 (4.45).

CI 7 Guaiazulene with p-Dimethylaminobenzaldehyde

A mixture of guaiazulene (400 mgs.), p-dimethylaminobenzaldehyde (300 mgs.), perchloric acid (0.5 ml.), and tetrahydrofuran (7 ml.) was heated to the boiling point and then allowed to cool to room temperature. After 90 minutes, 3-p-dimethylaminobenzylideneguaiazulenium perchlorate (42%) was filtered off as copper-coloured prisms. After recrystallisation from acetic acid it had m.p. 159-160°. The product was analysed without recrystallisation.

Found; C 67.2 H 6.7 N 3.4 Cl 8.2,

$C_{24}H_{28}ClNO_4$ requires 67.1 6.6 3.3 8.3%

λ max. (acetic acid) 647 (4.98).

CI 8 Guaiazulene with m-Hydroxybenzaldehyde

Guaiazulene (200 mgs.), m-hydroxybenzaldehyde (122 mgs.) and perchloric acid (0.5 ml.) in tetrahydrofuran (2 ml.), gave 3-m-hydroxybenzylideneguaiazulenium perchlorate as orange-red needles (242 mgs., 60%), which, after recrystallisation from acetic acid, had m.p. 203-211°(d).

Found; C 64.5 H 5.8 Cl 7.4,

$C_{22}H_{23}ClO_5$ requires 65.6 5.8 8.8%

λ max. (acetic acid) 475 (4.18).

CI 9 Guaiazulene with 2,4-Dihydroxybenzaldehyde

Guaiazulene (200 mgs.), 2,4-dihydroxybenzaldehyde (138 mgs.) and perchloric acid (0.5 ml.), allowed to react as in (CI 1) above, yielded 2,4-dihydroxybenzylideneguai-

azulenium perchlorate as dark red needles (82 mgs., 20%). After recrystallisation from acetic acid the m.p. was 207-210°(d).

Found; C 62.7 H 5.4 Cl 9.2,

$C_{22}H_{23}ClO_6$ requires 63.1 5.5 8.5%

λ max. (acetic acid) 563 (4.67).

CI 10 Guaiazulene with Piperonal

Guaiazulene (200 mgs.) and piperonal (150 mgs.), allowed to react as in (CI 1) above, yielded 3-piperonylidene-guaiazulenium perchlorate as crimson needles (176 mgs., 41%). After recrystallisation from acetic acid the m.p. was 236-240°(d).

Found; C 63.6 H 5.6 Cl 9.1,

$C_{23}H_{23}ClO_6$ requires 64.1 5.4 8.2%

λ max. 531 (4.43).

CI 11 Guaiazulene with p-Chlorobenzaldehyde

Guaiazulene (400 mgs.), p-chlorobenzaldehyde (280 mgs.) and perchloric acid (1 ml.) reacted as in (CI 1) to give p-chlorobenzylideneguaiazulenium perchlorate, as orange crystals of indefinite form (657 mgs., 80%), whose m.p., after recrystallisation from acetic acid, was 212-220°(d).

Found; C 63.0 H 5.4 Cl 16.5,

$C_{22}H_{22}Cl_2O_4$ requires 62.7 5.3 16.9%

λ max. 454 (4.00).

CI 12 Guaiazulene with m-Nitrobenzaldehyde

Guaiazulene (200 mgs.), m-nitrobenzaldehyde (150 mgs.), and perchloric acid (0.5 ml.) reacted under the same conditions as in (CI 1), to yield m-nitrobenzylideneguaiazulenium perchlorate, orange needles (304 mgs., 71%). After recrystallisation from acetic acid, the m.p. was 195-200°(d).

Found; C 61.2 H 5.2 N 3.2 Cl 8.3,

$C_{22}H_{22}ClNO_6$ requires 61.2 5.1 3.2 8.2%

λ max. 438 (3.97).

CI 13 Guaiazulene with p-Nitrobenzaldehyde

Guaiazulene (200 mgs.), p-nitrobenzaldehyde (150 mgs.), and perchloric acid (0.5 ml.) reacted as in (CI 1) above, yielding p-nitrobenzylideneguaiazulenium perchlorate, as orange needles (330 mgs., 76%). After recrystallisation from acetic acid the m.p. was 195-201°(d).

Found; C 60.7 H 4.8 N 3.3 Cl 7.6,

$C_{22}H_{22}ClNO_6$ requires 61.2 5.1 3.2 8.2%

λ max. (acetic acid) shoulder at 435 (3.74).

CI 14 Guaiazulene with 2-Furfuraldehyde

Guaiazulene (200 mgs.), 2-furfuraldehyde (96 mgs.), and perchloric acid (0.5 ml.) reacted as in (CI 1) above, yielding 2-furylideneguaiazulenium perchlorate, red needles (260 mgs., 69%). After recrystallisation from acetic acid the m.p. was 236-241°(d).

Found; C 63.6 H 6.1 Cl 10.2,

$C_{20}H_{21}ClO_5$ requires 63.7 5.6 9.4%

λ max. 505 (4.56).

CI 15 Guaiazulene with 2-Formylthiophen

Guaiazulene (200 mgs.), 2-formylthiophen (112 mgs.), and perchloric acid (0.5 ml.) reacted as in (CI 1) above to yield 3-(2-thienyl)methyleneguaiazulenium perchlorate, red needles (104 mgs., 27%). After recrystallisation from acetic acid the m.p. was 222-226°(d).

Found; C 61.2 H 5.3 Cl 9.1 S 8.5,

$C_{20}H_{21}ClO_4S$ requires 61.1 5.4 9.0 8.2%

λ max. 505 (4.53).

CI 16 Guaiazulene with 3-Formylindole

A mixture of guaiazulene (400 mgs.), 3-formylindole (290 mgs.), perchloric acid (1 ml.) and acetic acid (10 ml.) was heated to the boiling point and then allowed to cool to room temperature. 3-(3-Indolyl)methyleneguaiazulenium perchlorate (66%) w s obtained as violet-black needles, which, after recrystallisation from acetic acid decomposed > 242°.

Found; C 67.8 H 5.8 N 3.0 Cl 7.9,

$C_{24}H_{24}ClNO_4$ requires 67.7 5.9 3.3 8.3%

λ max. (acetic acid) 582 (4.10).

CI 17 Guaiazulene with 2-Formylpyridine

Guaiazulene (200 mgs.), 2-formylpyridine (107 mgs.),

and perchloric acid (0.5 ml.) reacted as in (CI 1) above. 3-(2-Pyridinium)methyleneguaiazulenium diperchlorate crystallised as orange needles after scratching and allowing the solution to stand at room temperature for 30 minutes, (87 mgs., 23%). After recrystallisation from acetonitrile--ethylmethyl ketone (1:2) the m.p. was 188-190.5°(d).

Found; C 51.9 H 5.2 N 2.6 Cl 14.8,

$C_{21}H_{23}Cl_2NO_8$ requires 51.6 4.8 2.9 14.5

λ max. (acetic acid) 410 (3.80).

CI 18 Guaiazulene with 4-Formylpyridine

Guaiazulene (200 mgs.), 4-formylpyridine (107 mgs.) and perchloric acid (0.5 ml.) reacted as in (CI 1) above, to yield 3-(4-pyridinium)methyleneguaiazulenium diperchlorate as yellowish-brown needles (267 mgs., 69%), whose m.p., after recrystallisation from acetonitrile-ethylmethyl ketone (1:5) was 195-198°(d).

Found; C 51.6 H 5.2 N 3.2 Cl 14.0,

$C_{21}H_{23}Cl_2NO_8$ requires 51.6 4.8 2.9 14.5%

λ max. (point of inflection) (acetic acid) 420 (3.70).

CI 19 Guaiazulene with 2-Formylquinoline

Guaiazulene (200 mgs.), 2-formylquinoline (157 mgs.), and perchloric acid (0.5 ml.) reacted as in (CI 1) to yield 3-(2-quinolinium)methyleneguaiazulenium diperchlorate as orange-red needles (421 mgs., 97%), which, after recrystallisation from acetonitrile-ethylmethyl ketone (1:2),

decomposed without melting above 210°.

Found;	C 55.5	H 4.7	N 1.2	Cl 13.3,
$C_{25}H_{25}Cl_2NO_8$ requires	55.8	4.7	2.6	13.2%

λ max. 425 (4.15).

CI 20 Guaiazulene with 4-Formylquinoline

Guaiazulene (200 mgs.), 4-formylquinoline monohydrate (175 mgs.), and perchloric acid (0.5 ml.) reacted as in (CI 1), yielding 3-(4-quinolinium)methyleneguaiazulenium diperchlorate, yellow needles (354 mgs., 78%), which, after recrystallisation from acetonitrile-ethylmethyl ketone (1:1), decomposed without melting above 203°.

Found;	C 55.1	H 4.5	N 2.4	Cl 13.2,
$C_{25}H_{25}NCl_2O_8$ requires	55.8	4.7	2.6	13.2%

λ max. (shoulder) (acetic acid) 435 (3.88).

CI 21 Azulene with p-Hydroxybenzaldehyde

A solution of azulene (128 mgs.) in acetic acid (15 ml.) was treated with a solution of p-hydroxybenzaldehyde (122 mgs.) and perchloric acid in acetic acid (15 ml.) at room temperature. After a few minutes the blood-red solution deposited a reddish-brown solid. 1-p-Hydroxybenzylideneazulenium perchlorate (205 mgs., 61%) was filtered off after 2 hours, washed with acetic acid followed by much ether, and dried in vacuo. M.p. 210-215° (d).

Found;	Cl 9.3,	
$C_{17}H_{13}ClO_5$ requires	10.7%	

λ max. (acetonitrile) 500.

CI 22 Azulene with p-Dimethylaminobenzaldehyde

Reaction was as in (CI 21), using the aldehyde (150 mgs.) in place of p-hydroxybenzaldehyde. Green crystals of 1-p-dimethylammoniumbenzylideneazulenium diperchlorate separated at once from the green solution. These were collected, washed with acetic acid, and on being suspended in water (25 ml.), immediately became blue. After being shaken for 30 minutes, to complete hydrolysis, the blue solid was filtered off, washed with water until free of acid, and dried in vacuo. 1-p-Dimethylaminobenzylideneazulenium perchlorate was thus obtained as blue crystals which melt to a blue tar on a block preheated to $< 210^{\circ}$.

Found;	C 66.4	H 5.4	N 4.7,
$C_{19}H_{18}ClNO_4$ requires	63.4	5.0	3.9%

λ max. (acetonitrile) 635.

CI 23 Azulene with 2-Furfuraldehyde

Azulene (192 mgs.), 2-furfuraldehyde (144 mgs.) and acetic acid (8 ml.) with perchloric acid (0.5 ml.) gave a bright red solution. 1-2'-Furylideneazulenium perchlorate (415 mgs., 90%) crystallised as orange needles, and, after being washed with acetic acid followed by much ether, it was dried for 20 minutes at 110°. M.p. 179-181° (block preheated to 175°).

Found;	C 56.1	H 3.9	Cl 12.4,
$C_{15}H_{11}ClO_5$ requires	58.8	3.6	11.6%

λ max. (acetonitrile) 496.

CI 24 Azulene with 3-Formylindole

A mixture of azulene (128 mgs.) and 3-formylindole (145 mgs.) in acetic acid (10 ml.), treated with perchloric acid (0.5 ml.), yielded 1-3'-indolylmethyleneazulenium perchlorate (305 mgs., 89%) as violet-black needles which were washed with acetic acid followed by ether, and dried for 20 minutes at 110°. The product melts to a violet liquid on a block preheated to $\leq$ 270°, but decomposes slowly to a black tar on being heated from room temperature.

	Found;	N 3.6	Cl 9.6,
$C_{18}H_{14}ClNO_4$	requires	4.1	10.3%

λ max. (acetonitrile) 560.

CI 25 4,6,8-Trimethylazulene with 2-Furfuraldehyde

A solution of 4,6,8-trimethylazulene (168 mgs.) and 2-furfuraldehyde (100 mgs.) in acetic acid (8 ml.) was treated with perchloric acid (0.5 ml.), at room temperature. The mixture turned brown, and crystallisation began at once. After 10 minutes, light brown needles of 1-(2-furyl)-methylene-4,6,8-trimethylazulenium perchlorate (35 mgs., 10%) were filtered off, washed with ether and dried in vacuo. Recrystallisation was from acetic acid. The product decomposed without melting above 200°.

	Found;	C 62.0	H 4.9	Cl 10.2,
$C_{18}H_{17}ClO_5$	requires	61.8	4.6	11.7%

CI 26 Guaiazulene with Acetaldehyde

The order of mixing of the reactants is critical, and the following is the most satisfactory procedure.

Perchloric acid (0.5 ml.) was added to a solution of guaiazulene (200 mgs.) and acetaldehyde (1.5 ml.) in tetrahydrofuran (1 ml.) at room temperature. 3-Ethylideneguaiazulenium perchlorate (310 mgs., 96%) crystallised after 1-2 minutes, as fine yellow needles. These were washed with tetrahydroguran followed by ether and dried in vacuo. M.p. 161-165°. The salt decomposes in hot solvents and was analysed without recrystallisation after drying for 8 hours at 70°/0.1 m.m.

Found; C 62.1 H 6.1 Cl 11.2,

$C_{17}H_{21}ClO_4$ requires 62.9 6.5 10.9%

λ max. (acetic acid) 425 (shoulder) (3.45), 370 (3.75).

CI 27 4,6,8-Trimethylazulene with Acetaldehyde

A solution of 4,6,8-trimethylazulene (763 mgs.) and acetaldehyde (3 ml.) in acetic acid (10 ml.) was treated with perchloric acid (1 ml.). 1-Ethylidene-4,6,8-trimethylazulenium perchlorate (1170 mgs., 88%) crystallised as greenish-yellow needles, which were washed with acetic acid followed by ether, and dried in vacuo. M.p. 148-151°(d). This was analysed without recrystallisation.

Found; C 60.7 H 6.0,

$C_{15}H_{17}ClO_4$ requires 60.7 5.8%

λ max. (acetonitrile) 405 (broad) (3.66).

λ max. (acetic acid) 440 (shoulder) (3.50).

λ max. (acetic acid containing 2% (v/v) perchloric acid) 395 (broad) (3.70).

CI 28 Guaiazulene with Cinnamaldehyde

Guaiazulene (200 mgs.) and cinnamaldehyde (132 mgs.), dissolved in tetrahydrofuran (2 ml.), and treated with perchloric acid (0.5 ml.) at room temperature, yielded 3-cinnamylideneguaiazulenium perchlorate (212 mgs., 50%) as dark red needles. After recrystallisation from acetic acid, the m.p. was 218-224°(d).

Found;	C 70.3	H 5.9	Cl 8.1,	
$C_{24}H_{25}ClO_4$ requires	69.8	6.1	8.6%	

λ max. (acetic acid) 513 (4.63).

CI 29 Guaiazulene with Phenylacetaldehyde

Phenylacetaldehyde (200 mgs.) was added to a mixture of guaiazulene (200 mgs.), tetrahydrofuran (1 ml.) and perchloric acid (0.5 ml.). A yellowish-brown semi-crystalline solid (85 mgs.), with m.p. 92-98°, was filtered off, washed with tetrahydrofuran and dried in vacuo. This product, however, could not be purified. The absorption spectrum (acetic acid) showed no maximum in the visible region, only a progressive slope upwards into the U.V. region.

Numerous variations to the experiment procedure with respect to the proportions of componants and order of mixing were tried without success. Nothing could be isolated after

boiling the reaction mixture.

CI 30 4,6,8-Trimethylazulene with Phenylacetaldehyde

A solution of 4,6,8-trimethylazulene (170 mgs.) and phenylacetaldehyde (120 mgs.) in acetic acid (5 ml.) was treated with perchloric acid (0.5 ml.). Yellowish-green needles were precipitated from the yellow solution by the addition of ether, but these rapidly decomposed.

CI 31 4,6,8-Trimethylazulene with Glyoxal

A mixture of 4,6,8-trimethylazulene (680 mgs.), glyoxal (345 mgs.), acetic acid (20 ml.), and perchloric acid (0.5 ml.) was heated to the boiling point, then allowed to cool to room temperature. The reddish-brown solution deposited the monoperchlorate (559 mgs., 60%) as green needles, which soften with decomposition above 257° on a block preheated to $\pm 250°$. This compound was unchanged in form, composition, or m.p., after recrystallisation from acetonitrile (10 ml./mg.).

Found; C 72.6 H 6.3 Cl 8.2,

$C_{28}H_{27}ClO_4$ requires 72.6 5.9 7.7%

λ max. (acetonitrile) 664 (4.71), 437 (4.20).

Solutions of this salt in polar organic solvents are violet-blue, but in the presence of excess perchloric acid they become reddish brown, and the solubility of the salt is increased.

Recrystallisation of the monoperchlorate from a 20%

(v/v) solution of perchloric acid in acetonitrile gave ethanediylidenebis(1'-4,6,8-trimethylazulenium)diperchlorate, as black needles, which soften 250° on a block preheated to 250°. These were washed with ether and dried in vacuo.

Found; C 58.9 H 7.0 Cl 12.2,

$C_{28}H_{28}Cl_2O_8$ requires 59.7 5.0 12.6%

λ max. (acetonitrile containing 2% (v/v) perchloric acid) 458 (4.48), 432 (4.43), 370 (4.31).

The monoperchlorate $C_{28}H_{27}ClO_4$ crystallises from solutions of the diperchlorate in acetonitrile alone.

CI 32 4,6,8-Trimethylazulene with Glyoxylic Acid

(i) A mixture of 4,6,8-trimethylazulene (680 mgs.), glyoxylic acid (183 mgs.) and acetonitrile (25 ml.) was refluxed for three minutes. The solution became blue, and, on cooling, deposited an acid (7 mgs.), as blue needles which melt with decomposition on a block preheated $\not<$ 308°.

λ max. (acetonitrile) 650. ν_{CO} (Nujol) 1701 cm^{-1}.

This acid decomposed after standing for two days in an evacuated desiccator.

The filtrates were diluted with ether (400 ml.) and the ether solution was exhaustively extracted with 10% sodium carbonate solution, washed with water, and dried (Na_2SO_4). 4,6,8-Trimethylazulene (221 mgs., 33%) was recovered after evaporation of the solvent. The sodium carbonate extracts, after being acidified, and extracted with ether, afforded a

blue solid (250 mgs.) which was readily soluble in polar solvents. Recrystallisation of the solid from petrol-ethanol (9:1) gave, in low yield, di(4,6,8-trimethylazulen-1-yl) acetic acid as blue crystals, m.p. 168-171°, after softening > 160°.

Found; C 83.3 H 7.5,

$C_{28}H_{28}O_2$ requires 84.8 7.1%

λ max. (acetonitrile) 595 (shoulder) (2.93), 560 (broad) (3.00).

ν_{CO} (Nujol) 1701 cm^{-1}.

(ii) A mixture of 4,6,8-trimethylazulene (340 mgs.), glyoxylic acid (184 mgs.), and acetonitrile (20 ml.), was boiled for 30 seconds with perchloric acid (0.2 ml.). After cooling, the solution was reddish brown, but no product could be isolated (C.f. the corresponding reaction with guaiazulene[176]).

CI 33 Azulene with Hydroxymethyleneacetone

A mixture of azulene (2091 mgs.), the sodium salt of hydroxymethyleneacetone (2095 mgs.), ethanol (50 ml.) and perchloric acid (1 ml.), was refluxed for 5 minutes. The blue solution was then poured into water (500 ml.) and extracted with ether. The ether extract was washed with sodium carbonate solution followed by water, before drying (Na_2SO_4) and evaporating the solvent. The residual blue oil was absorbed onto a column (20 x 2.5 cm.) from a small volume of benzene. Azulene (2040 mgs., 99%) was recovered by elution with light petrol. The yellowish-green ether eluates

from a weak brown band afforded a yellow oil (11 mgs., 0.3%), which failed to crystallise after further chromatography, but whose visible spectrum showed it to be azulen-1-ylmethylene-acetone. (See Plate IX).

λ max. (benzene) 603 (broad), 436.

ν_{CO} (CCl_4) 1672 cm^{-1}, with weaker bands at 1653 and 1678 cm^{-1}.

During a subsequent experiment using an excess of the sodium salt, an unidentified blue oil was isolated by slow elution of the chromatogram with benzene, after elution of azulen-1-ylmethyleneacetone.

λ max. (benzene) 652, 602.

ν_{CO} (CCl_4) 1715 cm^{-1}.

The blue material could not be crystallised after further chromatography, but readily gave a 2,4-dinitrophenylhydrazone with m.p. ~ 100°. There was, however, insufficient material for analysis.

CI 34 Guaiazulene with Hydroxymethyleneacetone

A mixture of guaiazulene (199 mgs.), the sodium salt of hydroxymethyleneacetone (112 mgs.) and acetic acid (5 ml.) was treated with perchloric acid (0.5 ml.) at room temperature. After 30 minutes the scarlet solution was poured into water and extracted with ether. The ether extract was worked up in the usual manner, and the residue obtained after evaporation of the solvent was adsorbed onto a column

(2.5 10 cm.) from the minimum volume of benzene. Guaiazulene (177 mgs., 90%) was recovered from the initial blue light petrol eluates. The succeeding ether eluates yielded guaiazulen-3-ylmethyleneacetone (18 mgs., 6%) as a yellowish-green oil which, owing to partial decomposition, could not be purified in sufficient quantity for analysis by distillation at ~ 160°/0.1 m.m.

λ max. (benzene) 604 (broad), 426 (broad).

CI 35 4,6,8-Trimethylazulene with Hydroxymethyleneacetone

A solution of 4,6,8-trimethylazulene (1250 mgs.), and the sodium salt of hydroxymethyleneacetone (794 mgs.) in ethanol (30 ml.) was treated with perchloric acid (1 ml.). The crimson solution was refluxed for 5 minutes, and another portion (400 mgs.) of the sodium salt added. Boiling was continued for a further five minutes, before the solution was poured into water (500 ml.) and extracted with ether. The ether solution was worked up in the usual manner, and the residue obtained after evaporation of the solvent was adsorbed onto a column (2.5 x 15 cm.) from the minimum volume of benzene. 4,6,8-Trimethylazulene (1238 mgs., 98%) was recovered from the initial purple light petrol eluates. Subsequent elution with ether gave a solution which was yellow in reflected light, and red in transmitted light. This yielded 4,6,8-trimethylazulen-1-ylacetone (17 mgs., 1%), which crystallised from cyclohexane as dark grey plates with

m.p. 111.5 - 113.5°(d).

Found; C 85.7 H 7.6

$C_{17}H_{18}O$ requires 87.5 7.5%

λ max. (cyclohexane) 567 (broad) (2.88), 405 (broad) (4.32).

CI 36 Azulene with Hydroxymethyleneacetophenone

Perchloric acid (1 ml.) was added to a boiling mixture of azulene (1081 mgs.), the sodium salt of hydroxymethylene-acetophenone (716 mgs.), and methanol (25 ml.). The solution became deep blue after refluxing for 10 minutes. On cooling, 1,1'-azulenylmethyleneazulenium perchlorate (347 mgs., 22%) crystallised as a blue powder (λ max. (acetic acid) 618 mμ.) which was identical with the product of condensation of azulene, 1-formylazulene, and perchloric acid (CII 1).

The methanol filtrate was diluted with ether (400 ml.) and a further small quantity (14 mgs., 0.9%) of precipitated dye-salt was removed. The ether solution was washed with 10% sodium hydroxide, solution followed by water, and dried (Na_2SO_4). After removal of the solvent, the residue was adsorbed onto a column (6 x 2.5 cm.) from the minimum volume of benzene. Azulene (521 mgs., 48%) was recovered from the violet-blue light petrol eluates after further chromatography on a second column (10 x 2.5 cm.) using light petrol as solvent and eluant. Subsequent elution of the original chromatogram with benzene gave green eluates (150 ml.) which,

after evaporation of the solvent, and treatment of the residual oil with Brady's reagent, gave acetophenone 2,4-dinitrophenylhydrazone, with m.p. and mixed m.p. 244 - 246°.

When the condensation was carried out in boiling acetic acid, the dye-salt was contaminated with a quantity of a sparingly soluble product of unknown structure (λ max. (acetic acid) 693 m.μ.).

CI 37 Guaiazulene with Hydroxymethyleneacetophenone

A boiling solution of guaiazulene (1995 mgs.), the sodium salt of hydroxymethyleneacetophenone (1700 mgs.) in acetic acid (25 ml.) was treated with perchloric acid (1 ml.). The resulting chocolate brown solution was boiled for 2 minutes, cooled, and diluted with ether. The ether solution was washed successively with water, sodium carbonate solution, and water, before drying (Na_2SO_4), and evaporation of the solvent. The residual dark yellowish-green oil was adsorbed onto a column (20 x 2.5 cm.) from a small volume of benzene. Guaiazulene (1365 mgs., 68%) was recovered from the blue light petrol eluates. The column was washed with a small quantity of benzene, then elution was continued with ether to give yellowish-green eluates. Evaporation yielded guaiazulen-3-ylmethyleneacetophenone (996 mgs., 30%) as a viscous brown oil which did not crystallise. Further attempted purification by two successive distillations at

220°/0.1 m.m. failed to give an analytically pure specimen.

Found; C 87.8 H 7.4,

$C_{24}H_{24}O$ requires 90.2 7.3%

λ max. (cyclohexane) 602 (2.40), 441 (3.94), 401 (4.09).

Treatment of the product with 2,4-dinitrophenylhydrazine hydrochloride in warm ethanol gave the 2,4-dinitrophenylhydrazone as brown needles. M.p., after recrystallisation from benzene, 243 - 247°.

Found; N 11.1,

$C_{30}H_{28}N_4O_4$ requires 11.0%

Treatment of guaiazulen-3-ylmethyleneacetophenone (200 mgs.) in acetic acid (25 ml.) with perchloric acid (1 ml.), afforded 3-(γ-hydroxycinnamylidene)guaiazulenium perchlorate (96 mgs., 36%), which recrystallised from acetic acid as dark red needles, with m.p. 209 - 211° (block preheated to 200°).

Found; Cl 8.9

$C_{24}H_{25}ClO_5$ requires 8.3%

CI 38 4,6,8-Trimethylazulene with Hydroxymethyleneacetophenone

4,6,8-Trimethylazulene (1170 mgs.), the sodium salt of hydroxymethyleneacetophenone (1170 mgs.) and acetic acid (25 ml.) were heated to 80°. Perchloric acid (0.5 ml.) was added, and the solution kept at 80° for 3 minutes. The reddish-brown solution was cooled, poured into water (600 ml.) and extracted with ether. The ether extracts, after being

washed with sodium carbonate solution followed by water, and dried (Na_2SO_4), were stripped of solvent. The residue was dissolved in the minimum volume of benzene and adsorbed onto a column (30 x 2.5 cm.). 4,6,8-Trimethylazulene (932 mgs., 81%) was recovered from the purple light petrol eluates. After washing of the column with benzene, a dark red zone was eluted with ether. The ether eluates, yellow in reflected and red in transmitted light, were concentrated, and the residual oil crystallised from petrol ethanol (20:1). Recrystallisation of the solid (269 mgs., 13%) from petrol ethanol (20:1) gave 4,6,8-trimethylazulen-1-ylacetophenone, brown needles, m.p. 142-144° (Lit.[71] m.p. 142-144°).

λ max. (cyclohexane) 563 (2.92), 424 (4.46).

ν_{CO} (Nujol) 1634 cm^{-1}.

CI 39 Azulene with 2-Hydroxymethylenecyclohexanone

(i) In Boiling Acetic Acid

A mixture of azulene (1081 mgs.), 2-hydroxymethylene-cyclohexanone (1061 mgs.), acetic acid (25 ml.) and perchloric acid (0.5 ml.) was boiled for 30 seconds. 1,1'-Azulenyl-methyleneazulenium perchlorate (1534 mgs., 99%) crystallised from the cooled solution as dark blue needles, identical spectrally (λ max. 618 mμ.) with an authentic specimen (CII 1).

In a second experiment using azulene (1648 mgs.), 2-hydroxymethylenecyclohexanone (808 mgs.), acetic acid (25 ml.), and perchloric acid (1 ml.), the dye-salt, obtained

in quantitative yield, was washed several times with ether and water alternately, and the mother liquor was shaken up with the ether washings. The ether phase was washed successively with water, 10% sodium hydroxide solution, and water. It was then dried (Na_2SO_4), and the solvent evaporated through a short Vigreux column. Cyclohexanone distilled ($< 80°/15$ m.m.) from the residual green oil, and was identified as its 2,4-dinitrophenylhydrazone, m.p., and mixed m.p. 154-156°.

(ii) <u>In Methanol at Room Temperature</u>

A mixture of azulene (1039 mgs.), 2-hydroxymethylene-cyclohexanone (1020 mgs.), and methanol (50 ml.), was treated with perchloric acid (0.5 ml.), giving a reddish-brown solution, which was allowed to stand at room temperature for five minutes, before being poured into water (400 ml.). The emulsion was shaken up with ether (500 ml.), and the resulting mixture was filtered from a trace (9 mgs., 0.6%) of 1,1'-azulenylmethyleneazulenium perchlorate (λ max. 618 m.μ.). The green ether phase was washed successively with water, 10% sodium hydroxide solution, and water, and dried (Na_2SO_4) before evaporation of the solvent. The residue was adsorbed onto a column (15 x 2.5 cm.) from a small volume of benzene. Azulene (54 mgs., 5%) was recovered from the initial violet-blue light petrol eluates. Subsequent elution of a strongly adsorbed brown band with ether gave

blue-green eluates, which, after evaporation of solvent, gave 2-(azulen-1-yl)methylenecyclohexanone (353 mgs., 19%) as a green oil.

λ max. (benzene) 612 (broad), 410.

The 2,4-dinitrophenylhydrazone recrystallised from benzene as dark green needles, m.p. 216-218°.

Found; N 12.9,

$C_{23}H_{20}N_4O_4$ requires 13.4%

CI 40 Guaiazulene with 2-Hydroxymethylenecyclohexanone

A mixture of guaiazulene (2440 mgs.), 2-hydroxymethylene-cyclohexanone (1542 mgs.), acetic acid (40 ml.), and perchloric acid (1.5 ml.) was refluxed for 3 minutes. The crimson solution was cooled and diluted with ether (500 ml.). A small amount of impure 3,3'-guaiazulenylmethyleneguaiazulenium perchlorate was precipitated as a black solid (40 mgs., λ max. 683 m.μ.). The ether filtrate was washed successively with water, sodium carbonate solution, and water, and dried (Na_2SO_4). After evaporation of the solvent, the residual oil was adsorbed onto a column (20 x 2.5 cm.) from a small volume of benzene. Guaiazulene (1279 mgs., 52%) was recovered from the blue light petrol eluates. Subsequent slow elution of a strongly adsorbed brown band with benzene--ether (1:1) yielded green eluates. 2-(Guaiazulen-3-yl)-methylenecyclohexanone (1529 mgs., 41%) was obtained as a green oil, which crystallised from a benzene solution, after

five weeks, as green prisms, m.p. 116.5-119.5°.

Found; C 86.3 H 8.5,

$C_{22}H_{26}O$ requires 86.2 8.6%

λ max. (benzene) 620 (broad) (2.73), 477 (broad) (4.30)

ν_{CO} (Nujol) 1667 cm^{-1}. (CCl_4) 1667 cm^{-1}.

The 2,4-dinitrophenylhydrazone recrystallised from benzene as reddish-brown needles, m.p. 212-216°, after softening > 209°.

Found; N 11.8,

$C_{28}H_{30}N_4O_4$ requires 11.5%

CI 41 <u>4,6,8-Trimethylazulene with 2-Hydroxymethylene-cyclohexanone</u>

A mixture of 4,6,8-trimethylazulene (1400 mgs.), 2-hydroxymethylenecyclohexanone (1037 mgs.), acetic acid (25 ml.), and perchloric acid (0.5 ml.), was refluxed for 2 minutes. The colour changed through scarlet to brownish red. The cooled solution deposited a viscous blue tar. The supernatent liquid was decanted from the tar, diluted with ether, and the sludge which precipitated, was extracted exhaustively with ether. After 12 hours a dark brown microcrystalline solid (164 mgs.) with m.p. ~ 150°(d), which had crystallised from the ether extracts, was filtered. Attempted purification of the solid by crystallisation failed. It was insoluble in ether, slightly soluble in benzene, and readily soluble in acetone or ethanol giving

purple solutions.

The tar which separated from the reaction solution was dissolved in acetone. Water (1 litre) was added, then ether (500 ml.) and the mixture thoroughly shaken up, and after standing overnight the mixture was filtered. Recrystallisation of the residual solid (14 mgs., 0.8%) from methanol gave 1-(4,6,8-trimethylazulen-1-yl)methylene-4,6,8-trimethylazulenium perchlorate (λmax. (acetic acid) 640 mμ.), identical with the product of condensation of 4,6,8-trimethylazulene with 1-ethoxymethylene-4,6,8-trimethylazulenium perchlorate (CVI 2). The ether layer was washed with water until free from an unidentified blue water soluble substance (λ max. (water) 593 mμ.); it was then reddish-brown and was combined with the ether filtrates remaining after filtration of the solid, m.p. 150°. The combined ether filtrates were washed successively with water, sodium carbonate solution, and water, and dried (Na_2SO_4). After evaporation of the solvent, the residue, dissolved in the minimum volume of benzene, was adsorbed onto a column (20 x 2.5 cm.). 4,6,8-Trimethylazulene (383 mgs., 27%) was recovered from the initial purple light petrol eluates. After washing the column with benzene, a brown band was eluted with ether, giving a reddish-green solution which deposited a crystalline solid after concentration. Recrystallisation from cyclohexane gave 2-(4,6,8-trimethyl-

azulen-1-yl)methylenecyclohexanone (599 mgs., 26%) as brown prisms, m.p. 151-152°.

Found; C 86.0 H 8.2,

$C_{20}H_{22}O$ requires 86.3 7.6%

λ max. (benzene) 562 (broad) 2.84, 408 (broad) (4.24).

ν_{CO} (Nujol) 1667 cm^{-1}.

CI 42 Guaiazulene with Hydroxymethylenephenylacetonitrile

A mixture of guaiazulene (1431 mgs.), hydroxymethylene-phenylacetonitrile (1034 mgs.), and acetic acid (25 ml.) was refluxed for 2 minutes. After cooling, the greenish-brown solution was shaken up with ether (200 ml.) and water (200 ml.). The ether extract was washed up in the usual way, and after evaporation of the solvent, the residual oil was adsorbed onto a column (2.5 x 20 cm.) from a small volume of benzene. Guaiazulene (793 mgs., 55%) was recovered from the blue light petrol eluates. Elution of a yellowish-green band with benzene gave an oil (1070 mgs., 45%) which, after further purification by filtration in benzene through a column (2.7 x 8 cm.), afforded 3-(2-cyano-2-phenylvinyl)guaiazulene as a yellowish brown oil which crystallised from ethanol as brown needles, m.p. 84-84.5°.

Found; C 88.4 H 7.2 N 4.3,

$C_{24}H_{23}N$ requires 88.6 7.1 4.3%

λ max. (benzene) 615 (2.87), 448 (4.47).

ν_{CN} (Nujol) 2188 cm^{-1}, (CCl_4) 2203 cm^{-1}.

3-(2-Cyano-2-phenylvinyl)guaiazulene was also obtained from a solution of guaiazulene (198 mgs.), hydroxymethylenephenylacetonitrile (149 mgs.), and perchloric acid (1 ml.) in acetic acid (2 ml.) which had been allowed to stand at room temperature for 4 hours, after it had been worked up in the usual way.

CI 43 4,6,8-Trimethylazulene with Hydroxymethylenephenylacetonitrile

Perchloric acid (0.5 ml.) was added to 4,6,8-trimethylazulene (1276 mgs.) and hydroxymethylenephenylacetonitrile (1080 mgs.) in hot acetic acid (25 ml.), and the mixture was boiled for 3 minutes. The colour changed through brownish-red to yellowish-brown. On cooling, the solution deposited 1,3-di(2-cyano-2-phenylvinyl)-4,6,8-trimethylazulene (597 mgs., 19%) as brown needles, unchanged in form after recrystallisation from benzene, m.p. 224-229°.

Found; C 87.5 H 5.9 N 6.5,

$C_{31}H_{24}N_2$ requires 87.7 5.7 6.6%

λ max. (benzene) 560 (broad) (3.05), 426 broad (4.40).

ν_{CN} (Nujol) 2191 cm^{-1} 2210?cm^{-1} (CCl_4) 2284 cm^{-1}, 2209 cm^{-1}.

The mother liquor, diluted with ether (400 ml.) deposited 4,6,8-trimethylazulenium perchlorate (911 mgs.) as light brown granular crystals. The ether filtrate was then worked up in the usual manner, and after evaporation of the solvent, the residue was adsorbed onto a column (2.5 x 15 cm.) from a

small volume of benzene. 4,6,8-Trimethylazulene (222 mgs.) was obtained from the purple light petrol eluates. The total quantity of recovered hydrocarbon was thus 795 mgs. (62%). A brown band was subsequently eluted with ether, and the brownish-green eluates yielded a further quantity (32 mgs., 0.9%) of 1,3-di(2-cyano-2-phenylvinyl)-4,6,8-trimethylazulene, m.p. 222-232°.

CII Condensation of 1-Formylazulenes with Azulenes in the Presence of Perchloric Acid

CII 1 1-Formylazulene with Azulene

Perchloric acid (0.5 ml.) was added to solution of 1-formylazulene (330 mgs.), and azulene (300 mgs.) in boiling acetic acid (10 ml.). 1,1'-Azulenylmethyleneazulenium perchlorate (770 mgs., 100%) started to separate from the deep blue boiling solution, and was filtered off from the cooled solution as a black powder, which, after recrystallisation from acetonitrile, decomposed above 350° (on block preheated to 350°).

Found; C 68.5 H 4.0 Cl 9.1,

$C_{21}H_{15}ClO_4$ requires 68.8 4.1 9.7%

λ max. (acetic acid) 618 (5.08).

CII 2 1-Formylazulene with 1-Methylazulene

Perchloric acid (0.4 ml.) was added to a solution of 1-formylazulene (310 mgs.) and 1-methylazulene (293 mgs.) in

acetic acid (10 ml.) at room temperature. The mixture turned deep greenish-blue, and crystallisation began at once. After 3 minutes 1-(3-methylazulen-1-yl)methyleneazulenium perchlorate (562 mgs., 74%) was filtered off as green needles, which, after recrystallisation from acetonitrile, explode on a block preheated to $< 350^{\circ}$.

Found; C 69.8 H 4.4 Cl 9.1,

$C_{22}H_{17}ClO_4$ requires 69.4 4.5 9.3%

λ max. (acetic acid) 634 (5.02).

CII 3 1-Formylazulene with Guaiazulene

Perchloric acid (0.3 ml.) was added to a boiling solution of 1-formylazulene (170 mgs.) and guaiazulene (227 mgs.) in acetic acid (6 ml.). Black needles started to separate from the boiling solution. 1-(Guaiazulen-3-yl)-methyleneazulenium perchlorate (405 mgs., 85%) was obtained as green needles, which, after recrystallisation from acetonitrile, had m.p. 199-200.5° (block preheated to 195°).

Found; C 71.1 H 5.6 Cl 8.2,

$C_{26}H_{25}ClO_4$ requires 71.5 5.8 8.1%

λ max. (acetic acid) 645 (4.98).

CII 4 1-Formyl-2-Methylazulene with 1,2-Dimethylazulene

Perchloric acid (0.25 ml.) was added to a boiling solution of 1-formyl-2-methylazulene (38 mgs.) and 1,2-dimethylazulene (37 mgs.) in acetic acid (2 ml.). After refluxing for 5 minutes, the dark green solution was cooled, and a dark blue

powder (9 mgs.) was precipitated by the addition of ether. This was presumably 1-(1,2-dimethylazulen-3-yl)methylene--2-methylazulenium perchlorate. It was recrystallised from acetonitrile, but there was insufficient material for analysis.

λ max. (acetonitrile) 655.

CII 5 1-Formyl-2-methylazulene with 2-Methylazulene

Perchloric acid (0.2 ml.) was added to a hot solution of 1-formyl-2-methylazulene (17 mgs.) and 2-methylazulene (14 mgs.) in acetic acid (2 ml.). A dark blue powder (5 mgs.) was filtered from the cooled dark greenish-blue solution, presumably 1-(2-methylazulen-1-yl)methylene-2--methylazulenium perchlorate. This was recrystallised from acetonitrile, but there was insufficient material for further characterisation.

λ max. (acetonitrile) 641.

CIII 1(3)-Hydroxymethyleneazulenium Perchlorates

CIII 1 1-Hydroxymethyleneazulenium Perchlorate

A solution of 1-formylazulene (173 mgs.) in acetic acid (5 ml.) was treated with perchloric acid (0.5 ml.) at room temperature. Addition of dry ether caused crystallisation of 1-hydroxymethyleneazulenium perchlorate (284 mgs., 100%) as golden-yellow plates. The salt decomposes slowly > 140°, after recrystallisation from acetonitrile. Work must be as rapid as possible to avoid the hydrolysis which occurs

in air.

Found;	C 48.1	H 4.1	Cl 12.4,
$C_{11}H_9ClO_5$ requires	51.5	3.5	13.3%

CIII 2 3-Hydroxymethyleneguaiazulenium Perchlorate

A solution of 3-formylguaiazulene (211 mgs.) in acetic acid (5 ml.) was treated with perchloric acid (0.5 ml.). 3-Hydroxymethyleneguaiazulenium perchlorate (300 mgs., 100%) separated at once as yellow needles, which, after recrystallisation from acetonitrile-ethylmethyl ketone (1:2), melt at 158-160°, to a green liquid.

Found;	C 58.8	H 6.1	Cl 11.0
$C_{16}H_{19}ClO_5$ requires	58.8	5.9	10.9%

CIV Condensation of 1-Formyl-4,6,8-trimethylazulene with Heterocyclic Quarternary Ammonium Salts in the Presence of Piperidine

General Procedure

A mixture of 1-formyl-4,6,8-trimethylazulene (0.003 mole), the heterocyclic quarternary ammonium salt (0.003 mole), ethanol (25 ml.), and a small volume of piperidine was boiled for 5 minutes. In most cases the product partly crystallised from the boiling solution. It was filtered off from the cooled solution, and, unless otherwise stated, recrystallised from acetonitrile.

CIV 1 1-Formyl-4,6,8-trimethylazulene with 1,2-Dimethylpyridinium Perchlorate

2 Ml. of piperidine was used in the above procedure. 1-Methyl-2(2-(4,6,8-trimethylazulen-1-yl)vinyl)pyridinium perchlorate (43%) was obtained as dark brown needles, m.p. 264.5-271.5° (d).

Found; C 65.0 H 5.7 Cl 9.7 N 3.8,

$C_{21}H_{22}ClNO_4$ requires 65.0 5.7 9.1 3.6%

λ max. (Methanol) 482 (broad) (4.59).

CIV 2 1-Formyl-4,6,8-trimethylazulene with 1,2-Dimethylpyridinium Iodide

2 Ml. of piperidine was used. 1-Methyl-2-(2-(4,6,8-trimethylazulen-1-yl)vinyl)pyridinium iodide (42%) was isolated as dark brown needles, m.p. 257.5-259.5°(d).

Found; C 60.8 H 5.5 I 31.1 N 3.6,

$C_{21}H_{22}IN$ requires 60.7 5.3 30.6 3.4%

λ max. (methanol) 482 (broad) (4.59).

CIV 3 1-Formyl-4,6,8-trimethylazulene with 2,3-Dimethylbenzoxazolium Perchlorate

0.25 Ml. of piperidine was used. 3-Methyl-2-(4,6,8-trimethylazulen-1-yl)vinyl)benzoxazolium perchlorate (3%) was isolated as reddish-brown crystals of indefinite form. After washing the product with hot water and recrystallising it from ethanol, the m.p. was 285-290°(d).

Found; C 64.9 H 5.3 N 3.3,

$C_{23}H_{22}ClNO_5$ requires 64.6 5.2 3.3%

λ max. (methanol) 497 (4.76).

CIV 4 1-Formyl-4,6,8-trimethylazulene with 2,3,4-Trimethylthiazolium Perchlorate

1 Ml. of piperidine was used. 3,4-Dimethyl-2-(2-(4,6,8-trimethylazulen-1-yl)vinyl)thiazolium perchlorate (74%) was obtained as dark green needles, m.p. 296.5-301.5°(d).

Found;	C 59.9	H 5.8	Cl 8.2	N 3.2	S 7.6,	
$C_{20}H_{22}ClNO_4S$ requires	58.9	5.4	8.7	3.4	7.9%	

λ max. (methanol) 499 (4.61).

CIV 5 1-Formyl-4,6,8-trimethylazulene with 2,3,4-Trimethylthiazolium Iodide

1 Ml. piperidine was used. 3,4-Dimethyl-2-(2-(4,6,8-trimethylazulen-1-yl)vinyl)thiazolium iodide (74%) was isolated as dark green needles, m.p. 268-270°(d).

Found;	C 55.5	H 5.1	N 3.1,	
$C_{20}H_{22}INS$ requires	55.2	5.1	3.2%	

λ max. (methanol) 499 (4.59).

CIV 6 1-Formyl-4,6,8-trimethylazulene with 2,3-Dimethylthiazolium Perchlorate

0.5 Ml. piperidine was used. 3-Methyl-2-(2-(4,6,8-trimethylazulen-1-yl)vinyl)thiazolium perchlorate (56%) was obtained as purple needles, m.p. 270-274°(d).

Found;	C 57.9	H 5.1	Cl 9.1	N 3.6	S 8.0	
$C_{19}H_{20}ClNO_4S$ requires	57.9	5.1	9.0	3.6	8.1%	

λ max. (methanol) 499 (4.61).

CIV 7 1-Formyl-4,6,8-trimethylazulene with 1,4-Dimethylpyridinium Perchlorate

2 Ml. piperidine was used. 1-Methyl-4-(2-(4,6,8-trimethylazulen-1-yl)vinyl)pyridinium perchlorate (79%) was obtained as dark green needles, m.p. 271-274°(d).

Found; C 65.2 H 5.7 Cl 9.1 N 3.8,

$C_{21}H_{22}ClNO_4$ requires 65.0 5.7 9.1 3.6%

λ max. (methanol) 499 (4.64).

CIV 8 1-Formyl-4,6,8-trimethylazulene with 1,4-Dimethylpyridinium Iodide

2 Ml. piperidine was used. 1-Methyl-4-(2-(4,6,8-trimethylazulen-1-yl)vinyl)pyridinium iodide (75%) was obtained as dark green needles. It did not melt < 340°.

Found; C 60.5 H 5.2 I 30.8 N 3.5,

$C_{21}H_{22}IN$ requires 60.7 5.3 30.6 3.4%

λ max. (methanol) 499 (4.64).

CIV 9 1-Formyl-4,6,8-trimethylazulene with 2,3-Dimethylbenzothiazolium Perchlorate

0.5 Ml. piperidine was used, and 50 ml. ethanol was necessary for complete solution. The mixture was concentrated to 25 ml. before allowing it to crystallise. 3-Methyl-2-(2-(4,6,8-trimethylazulen-1-yl)vinyl)benzothiazolium perchlorate (59%) was obtained as deep purple needles, m.p. 276-277°.

Found; C 62.6 H 5.2 Cl 7.7 N 3.2 S 7.2,

$C_{23}H_{22}ClNO_4S$ requires 62.2 5.0 8.0 3.2 7.2%

λ max. 530 (4.74).

CIV 10 1-Formyl-4,6,8-trimethylazulene with 1,2-Dimethylquinolinium Perchlorate

0.5 Ml. of piperidine was used. 1-Methyl-2(2-(4,6,8--trimethylazulen-1-yl)vinyl)quinolinium perchlorate (63%) formed deep purple needles, which, after recrystallisation from acetonitrile-ethanol (1:4) soften slowly > 235°.

Found; Cl 8.2 N 3.1,

$C_{25}H_{24}ClNO_4$ requires 8.1 3.2%

λ max. methanol 567 (4.22).

CIV 11 1-Formyl-4,6,8-trimethylazulene with 1,4-Dimethylquinolinium Iodide

0.5 Ml. piperidine was used. 1-Methyl-4-(2-(4,6,8--trimethylazulen-1-yl)vinyl)quinolinium iodide (43%) was isolated as dark brown needles which soften > 350°.

Found; C 64.6 H 5.4 N 3.2,

$C_{25}H_{24}IN$ requires 64.5 5.2 3.0%

λ max. (methanol) 572 (4.63).

CV Condensation of Azulenes with Ethyl Orthoformate in the Presence of Strong Acids

CV 1 Azulene with Ethyl Orthoformate and Perchloric Acid

To a solution of azulene (512 mgs.) and ethyl orthoformate (10 ml.) in ethanol (25 ml.), at room temperature, perchloric

acid (1 ml.) was added. The mixture turned deep blue and immediately deposited 1,1'-azulenylmethyleneazulenium perchlorate (706 mgs., 96%) as dark needles, which, after recrystallisation from acetonitrile, decompose > 350° (on block preheated to 350°). This product was identical with that from the condensation of 1-formylazulene with azulene and perchloric acid (CII 1).

λ max. (acetic acid containing 0.4% (v/v) acetonitrile) 618 (5.08).

CV 2 1-Methylazulene with Ethyl Orthoformate and Perchloric Acid

A solution of perchloric acid (2.5 ml.) in ethanol (15 ml.) was added to a solution of 1-methylazulene (1.42 gms.) and ethyl orthoformate (15 ml.) in ethanol (30 ml.), at room temperature. 1-(3-Methylazulen-1-yl)methylene-3-methylazulenium perchlorate (3.83 gms., 97%) crystallised at once as green needles, which, after recrystallisation from acetonitrile, explode on a block preheated to ≮ 350°. This product was identical with that from the condensation of 1-formyl-3-methylazulene with 1-methylazulene and perchloric acid[191].

λ max. (acetic acid) 652 (5.01).

CV 3 2-Methylazulene with Ethyl Orthoformate and Perchloric Acid

A solution of 2-methylazulene (927 mgs.) in ethanol

(20 ml.), and ethyl orthoformate (12 ml.) was treated with a solution of perchloric acid (3 ml.) in ethanol (20 ml.), at room temperature. The mixture turned dark brown, but no crystalline material could be isolated. After five minutes the mixture was thoroughly shaken up with acetone-water (200 ml.) (1:1), and then diluted with a further 700 ml. water, and extracted with ether (3 x 200 ml.). A small amount of precipitated dye-salt was filtered from the extracts (λ max. (acetic acid) 641 m.μ.). The combined ether extracts were washed successively with water, sodium carbonate solution, and water. After drying (Na_2SO_4), and evaporation of the solvent, the brownish red residue was adsorbed onto a column (2.5 x 30 cm.) from a small volume of ether. A trace of 2-methylazulene was recovered from the blue light petrol eluates. Subsequent elution with ether yielded a small amount of unidentified yellow material, followed by dark red eluates, which afforded 1-formyl-2-methylazulene (425 mgs., 38%) as a dark red crystals after two distillations at ~100°/0.1 m.m., m.p. 77-80°.

Found; C 82.2 H 6.2,

$C_{12}H_{10}O$ requires 84.7 5.9%

λ max. (petrol) 532.

CV 4 1,2-Dimethylazulene with Ethyl Orthoformate and Perchloric Acid

A solution of 1,2-dimethylazulene (6.4 mgs.) in ethanol

(0.5 ml.), and ethyl orthoformate (1 ml.), was treated with perchloric acid (3 drops), at room temperature. 1-Ethoxymethylene-2,3-dimethylazulenium perchlorate (6 mgs., 47%) was obtained as orange needles, which, after being washed with ethanol followed by ether, had m.p. 174.5-181.5°(d). There was insufficient material for analysis.

A small quantity of 1-ethoxymethylene-2,3-dimethylazulenium perchlorate was hydrolysed with aqueous acetone, and worked up in the manner described in CV 3, giving a trace of 1-formyl-2,3-dimethylazulene as a red oil.

λ max. (petrol) 550.

CV 5 4,6,8-Trimethylazulene with Ethyl Orthoformate and Perchloric Acid

(i) A mixture of 4,6,8-trimethylazulene (1700 mgs.), ethanol (30 ml.), and ethyl orthoformate (15 ml.) was treated with a solution of perchloric acid (2.5 ml.) in ethanol (15 ml.), at room temperature. 1-Ethoxymethylene-4,6,8-trimethylazulenium perchlorate (3050 mgs., 94%) crystallised at once as yellow needles, and was filtered off, washed with ethanol followed by ether, and dried in vacuo. M.p. 141-146°, to a green liquid. The product was analysed without recrystallisation.

Found;	C 58.8	H 6.1	Cl 10.8,
$C_{16}H_{19}ClO_5$ requires	58.8	5.9	10.9%

1-Ethoxymethylene-4,6,8-trimethylazulenium perchlorate (3050 mgs.) was shaken vigorously with 400 ml. acetone-water

(1:1), then diluted with water (1 litre) and the mixture extracted with ether (2 x 350 ml.). The combined ether extracts were washed successively with water, sodium carbonate solution, and water, and dried (Na_2SO_4). After the solution had been concentrated, 1-formyl-4,6,8-trimethylazulene (1830 mgs., 99%) crystallised as red needles, which, after one recrystallisation from ethanol, had m.p. 105-106° (Lit.[71] 106-107°).

ν_{CO} (Nujol) 1618 cm^{-1}.

(ii) A mixture of 4,6,8-trimethylazulene (3400 mgs.), ethanol (60 ml.) and ethyl orthoformate (24 ml.) was treated with a solution of perchloric acid (5 ml.) in ethanol (30 ml.). The mixture became bluish-purple and deposited a small amount of solid material. The whole mixture was shaken with 400 ml. acetone-water (1:1) and then diluted and extracted with ether. The ether solution was washed successively with water, sodium carbonate solution, and water, and dried (Na_2SO_4). After evaporation of the solvent, the residue was adsorbed onto a column (2.5 x 20 cm.) from a small volume of light petrol. 4,6,8-Trimethylazulene (2990 mgs., 88%) was recovered from the initial purple light-petrol eluates. A red band, subsequently eluted with ether, yielded 1-formyl-4,-6,8-trimethylazulene (196 mgs.) as red needles. This corresponds to 5% conversion of 4,6,8-trimethylazulene into 1-ethoxymethylene-4,6,8-trimethylazulenium perchlorate.

CV 6 4,8-Dimethyl-6-phenylazulene with Ethyl Orthoformate and Perchloric Acid

A mixture of 4,8-dimethyl-6-phenylazulene (1046 mgs.), ethanol (10 ml.) and ethyl orthoformate (25 ml.), was treated with perchloric acid (1 ml.) at room temperature. 1-Ethoxymethylene-4,8-dimethyl-6-phenylazulenium perchlorate (1370 mgs., 78%) crystallised as brownish-yellow needles from the muddy-yellow solution, and was filtered off, washed with much ether, and dried in vacuo. M.p. 209-211°(d) (block preheated to ∠ 165°). A sample for analysis was dried at 60°/0.1 m.m. for 6 hours.

Found; C 65.2 H 5.4 Cl 9.1,

$C_{21}H_{21}ClO_5$ requires 64.9 5.4 9.1%

λ max. (acetonitrile) 455 (3.82).

1-Ethoxymethylene-4,8-dimethyl-6-phenylazulenium perchlorate (1110 mgs.), was hydrolysed by shaking it with 200 ml. acetone-water (1:1). The mixture was then diluted with water (1 litre), and extracted with ether. The ether extracts were worked up in the usual way, and after removal of the solvent, the residue was adsorbed onto a column (2.5 x 20 cm.) from a small volume of benzene. After the column had been washed with light petrol, a red band was eluted with ether, which yielded 1-formyl-4,8-dimethyl-6-phenylazulene (731 mgs., 98%) as crimson needles. After one recrystallisation it had m.p. 105-108°.

Found; C 87.7 H 6.3,

$C_{19}H_{16}O$ requires 87.7 6.2%

λ max. (benzene) 526 (broad) (2.87) 533 (broad) (2.87).

ν_{CO} (Nujol) 1631 cm^{-1}.

CV 7 4,8-Dimethyl-6-methoxyazulene with Ethyl Orthoformate and Perchloric Acid

A mixture of 4,8-dimethyl-6-methoxyazulene (1009 mgs.), ethanol (15 ml.), and ethyl orthoformate (25 ml.) was treated with perchloric acid (1 ml.). The solution instantly deposited 1-ethoxymethylene-4,8-dimethyl-6-methoxyazulenium perchlorate (1684 mgs., 90%) as yellow needles, which were filtered off, washed with much ether, and dried in vacuo. It had m.p. 165-173°(d), or 199-200°(d) on a block preheated to 170°.

Found; C 55.5 H 5.6 Cl 10.2,

$C_{16}H_{19}ClO_6$ requires 56.1 5.6 10.3%

λ max. (acetonitrile) 438 (3.79).

1-Ethoxymethylene-4,8-dimethyl-6-methoxyazulenium perchlorate (1414 mgs.) was hydrolysed by shaking with acetone--water (1:1) (200 ml.) and working up the mixture in the same way as described in (CV 6). The chromatogram (2.5 x 20 cm.) was first eluted with light petrol-benzene (1:1), and 4,8-dimethyl-6-methoxyazulene (53 mgs., 4%) was recovered from the scarlet eluates. An orange band was subsequently

eluted with ether and gave 1-formyl-4,8-dimethyl-6-methoxy-azulene (665 mgs., 72%) as orange needles. After recrystallisation from ethanol it had m.p. 124-125°.

Found; C 79.1 H 6.8,

$C_{14}H_{14}O_2$ requires 78.5 6.6%

λ max. (benzene) 481 (2.94).

ν_{CO} (Nujol) 1618 cm^{-1}.

CV 8 4,6-Diphenyl-8-methylazulene with Ethyl Orthoformate and Perchloric Acid

A mixture of 4,6-diphenyl-8-methylazulene (1317 mgs.), ethanol (10 ml.) and ethyl orthoformate (25 ml.) was treated with perchloric acid (1 ml.) at room temperature. The solution turned yellow and started to deposit crystals at once, but these subsequently became tarry, and no pure product could be isolated.

The mixture was hydrolysed by shaking it with 400 ml. acetone-water (1:1), and was then worked up in the same way as described in (CV 6). The chromatogram (2.5 x 20 cm.) was washed with light petrol, and then eluted with progressively more polar solvent mixtures. A purple band, eluted with benzene followed by benzene-ether (3:1), yielded 1-formyl-4-methyl-6,8-diphenylazulene and/or 1-formyl-4,6--diphenyl-8-methylazulene (1070 mgs., 74%) as a purple glassy mass. No further resolution of the product by chromatography could be obtained.

λ max. (benzene) 548.

ν_{CO} (Nujol) 1629 cm.$^{-1}$.

CV 9 4,6,8-Trimethylazulene with Ethyl Orthoformate and Hydrogen Bromide

A solution of hydrogen bromide in acetic acid (0.5 ml.), in dry ethanol (3 ml.), was added to a solution of 4,6,8-trimethylazulene (340 mgs. 0.002 mole), and ethyl orthoformate (5 ml., 0.03 mole, 1400% excess) in dry ethanol (3 ml.) at room temperature. 1-Ethoxymethylene-4,6,8-trimethylazulenium bromide (308 mgs., 50%) crystallised at once from the green solution, and was filtered off, washed with dry ethanol followed by ether, and dried at 100° for 5 minutes. Work must be as rapid as possible since hydrolysis occurs in air, especially in the presence of solvents. The m.p. after recrystallisation from acetonitrile (green prisms) was 146-150°(d).

	Found;	C 62.1	H 5.7,
$C_{16}H_{19}BrO$	requires	62.5	6.2%

CV 10 4,6,8-Trimethylazulene with Ethyl Orthoformate, Hydrogen Bromide, and Sodium Iodide

Hydrogen bromide in acetic acid (0.5 ml.), dissolved in dry ethanol (4 ml.) was added to a cold solution of 4,6,8-trimethylazulene (340 mgs., 0.002 mole), ethyl orthoformate (5 ml., 0.03 mole, 1400% excess), and anhydrous

sodium iodide (700 mgs.) in dry ethanol (10 ml.). 1-Ethoxymethylene-4,6,8-trimethylazulenium iodide (700 mgs., 100%) was deposited at once as brown needles, m.p. 145-150° (d). The product was filtered off, washed with ethanol followed by ether, and dried in vacuo. It was analysed without recrystallisation owing to decomposition in hot solvents.

Found; C 53.3 H 5.3,

$C_{19}H_{19}IO$ requires 54.3 5.4%

Note: When an identical experiment was performed, in which the mixture was heated to the boiling point, the colour deepened and 1-(4,6,8-trimethylazulen-1-yl)methylene-4,6,8--trimethylazulenium iodide (59 mgs., 13%) was isolated. After recrystallisation from methanol it decomposed > 200°. Analytical data were unsatisfactory.

Found; C 64.7 H 5.4 I 30.3,

$C_{27}H_{27}I$ requires 67.8 5.7 26.5

λ max. (acetic acid) 640 (4.96).

CVI Condensation of Azulenes with 1-Ethoxymethylene-4,6,8--trimethylazulenium Perchlorate

CVI 1 Azulene with 1-Ethoxymethylene-4,6,8-trimethyl-azulenium Perchlorate

A mixture of azulene (199 mgs.), 1-ethoxymethylene-4,6,8--trimethylazulenium perchlorate (500 mgs.), and methanol

(25 ml.) was boiled under reflux for 5 minutes. On cooling, 1-(4,6,8-trimethylazulen-1-yl)methyleneazulenium perchlorate (315 mgs., 50%) was filtered off and washed with methanol. Recrystallisation from acetonitrile gave dark blue needles which decompose $> 270^{\circ}$.

Found; C 69.8 H 5.7 Cl 8.8,

$C_{24}H_{21}ClO_4$ requires 70.5 5.2 8.7%

λ max. (acetic acid containing 4% (v/v) acetonitrile) 627 (5.00).

CVI 2 4,6,8-Trimethylazulene with 1-Ethoxymethylene-4,6,8--trimethylazulenium Perchlorate

A mixture of 4,6,8-trimethylazulene (148 mgs.), 1-ethoxymethylene-4,6,8-trimethylazulenium perchlorate (258 mgs.), and methanol (10 ml.) was boiled for five minutes, then cooled and filtered. 1-(4,6,8-Trimethylazulen-1-yl)-methylene-4,6,8-trimethylazulenium perchlorate (81 mgs., 20%) was obtained as dark needles, which, after recrystallisation from methanol, decompose $> 300^{\circ}$.

Found; C 72.2 H 6.2 Cl 8.5,

$C_{27}H_{27}ClO_4$ requires 71.9 6.0 7.9%

λ max. (acetic acid) 640 (4.94).

CVI 3 Guaiazulene with 1-Ethoxymethylene-4,6,8-trimethyl-azulenium Perchlorate

A mixture of guaiazulene (210 mgs.), 1-ethoxymethylene--4,6,8-trimethylazulenium perchlorate (327 mgs.), and

methanol (10 ml.), boiled for 5 minutes, became deep blue. After the solution had stood at room temperature for 1 hour, 1-(guaiazulen-3-yl)methylene-4,6,8-trimethylazulenium perchlorate (100 mgs., 20%) was filtered off as dark blue needles, and recrystallised from methanol. M.p. 217-219°.

Found; C 72.1 H 6.7 Cl 7.3,

$C_{29}H_{31}ClO_4$ requires 72.8 6.5 7.4%

λ max. (acetic acid) 653 (4.93).

CVII Azulenium Perchlorates

CVII 1 4,6,8-Trimethylazulenium Perchlorate

A solution of 4,6,8-trimethylazulene (538 mgs.) in acetic acid (12.5 ml.) was heated to the boiling point and treated with perchloric acid (0.3 ml.). After refluxing it for three minutes, the yellowish-red solution was cooled and diluted with dry ether (500 ml.). 4,6,8-Trimethylazulenium perchlorate (665 mgs., 77%) was deposited as light brown granular crystals, m.p. 168-171° (block preheated to 140°). It could not be recrystallised, since it breaks down in those solvents in which it is soluble (e.g. ethanol, or acetonitrile) to reform 4,6,8-trimethylazulene and perchloric acid. 4,6,8-Trimethylazulene (83 mgs., 16%) was recovered from the mother liquor in the usual way.

Found; C 57.2 H 5.6 ClO_4* 37.1,

$C_{13}H_{15}ClO_4$ requires 57.1 5.6 36.8%

* A quantitative hydrolysis experiment was performed by shaking the perchlorate (383 mgs.) with 200 ml. of light petrol-water mixture (1:1) until it had all decomposed. The phases were then separated, and each washed with the other solvent. The light petrol solution was dried (Na_2SO_4) and filtered through a column (2.5 x 4 cm.). Evaporation of the solvent left 4,6,8-trimethylazulene (238 mgs., 99.6%), identical (m.p. and mixed m.p.) with an authentic specimen. The aqueous layer was titrated against standard alkali using bromothymol blue as indicator; 383 mgs. of salt gave a solution requiring 17.0 ml. of 0.084N sodium hydroxide solution for neutralisation. From these data, ClO_4 = 37.1%.

CVII 2 Reaction of 4,6-Diphenyl-8-methylazulene with Perchloric Acid

4,6-Diphenyl-8-methylazulene was allowed to react in the same way as 4,6,8-trimethylazulene in (CVII 1), the operation being carried out in an atmosphere of dry nitrogen. A small quantity (4.3%) of product crystallised as green needles on the addition of perchloric acid, and a further quantity (3%) did so after dilution of the reaction mixture with ether. Both crops were impure, however, and no satisfactory analysis was obtained

CVII 3 4,8-Dimethyl-6-phenylazulenium Perchlorate

Perchloric acid (0.5 ml.) was added to a boiling mixture of 4,8-dimethyl-6-phenylazulene (498 mgs.) in acetic

acid (20 ml.). 4,8-Dimethyl-6-phenylazulenium perchlorate (450 mgs., 63%) crystallised at once as dark green needles, which, after recrystallisation from acetonitrile, melted at 240-245°(d) (block preheated to 230°).

Found; C 65.1 H 5.5 ClO_4* 30.0,

$C_{18}H_{17}ClO_4$ requires 65.0 5.2 30.2%

λ max. (acetonitrile) 580 (broad) (2.11), 3.71 (4.20). λ max. (acetonitrile containing 0.8% (v/v) perchloric acid) 377 (4.34).

4,8-Dimethyl-6-phenylazulene (57 mgs., 11%) was recovered from the mother liquors after these had been worked up in the usual way.

* A quantitative hydrolysis experiment was performed in the same way as described in (CVII 1), and gave recovered 4,8-dimethyl-6-phenylazulene (98.3%).

CVII 4 4,8-Dimethyl-6-methoxyazulenium Perchlorate

A solution of 4,8-dimethyl-6-methoxyazulene (429 mgs.) in acetic acid (25 ml.) was warmed, and treated with perchloric acid (0.5 ml.). The resulting pale yellow solution was cooled and diluted with dry ether (75 ml.). 4,8-Dimethyl-6-methoxyazulenium perchlorate (594 mgs., 90%) was deposited as colourless needles, which were washed with ether followed by petrol, and dried in vacuo. The salt could not be recrystallised without decomposition; it had m.p. 142-144° (block preheated to 130°).

Found; C 54.4 H 5.7 ClO_4* 35.4,

$C_{13}H_{15}ClO_5$ requires 54.4 5.3 35.0%

λ max. (acetonitrile containing 0.4% (v/) perchloric acid) 356 (4.35).

Working up the mother liquor in the usual way yielded unreacted 4,8-dimethyl-6-methoxyazulene (23 mgs., 5%).

* A quantitative hydrolysis experiment was performed in the same way as described in (CVII 1), and gave recovered 4,8-dimethyl-6-methoxyazulene (99.0%).

CVIII Reaction of Azulenes with Triarylmethyl Perchlorates

CVIII 1 Reaction of 1-Methylazulene with Triphenylmethyl Perchlorate

(i) Using an excess of 1-Methylazulene

A solution of 1-methylazulene (356 mgs., 0.0026 moles.) and triphenylmethyl perchlorate (169 mgs., 0.00049 moles.) in acetic acid (8 ml.) was refluxed for 90 seconds. It turned deep blue, while dark needles precipitated. The mixture was cooled, and, after half an hour, filtered to give 1-(3-methylazulen-1-yl)methylene-3-methylazulenium perchlorate (159 mgs., 82%). Recrystallisation from acetonitrile gave green needles, m.p. 350°(d) (block preheated to $<$ 350°).

Found; C 70.0 H 4.9 Cl 9.1,

$C_{23}H_{19}ClO_4$ requires 70.0 4.9 9.0%

λ max. (acetic acid) 652 (4.94).

The mother liquor from this reaction was diluted with light petrol (200 ml.), and decanted from a small amount of insoluble blue oil. After being washed with water, the

solution was extracted with Conc. HCl. until the acid extracts were colourless (6 x 50 ml.). The light petrol remained pale blue-green. The combined acid extracts, after being washed twice with light petrol, were diluted with water (1 litre), and extracted with light petrol (2 x 100 ml.). This light petrol solution was washed with water until free from acid, then dried (Na_2SO_4) and concentrated to small volume before filtration through a column (2.5 x 7 cm.) using light petrol as solvent and eluant. After removal of the solvent, using a short Vigreux column for the last 25 ml., a blue oil (177 mgs.) remained. Analysis by gas--chromatography showed it to consist of 1-methylazulene (85%), azulene (10%), and an unknown component (5%), with low retention time (1 minute).

During a similar experiment under the same conditions, triphenylmethane was isolated in a yield comparable to that of the dye-salt[192].

(ii) Using an excess of Triphenylmethyl Perchlorate

A solution of 1-methylazulene (401 mgs., 0.0028 moles.) in acetic acid (40 ml.) was added dropwise over 10 minutes, to a stirred and refluxing solution of triphenylmethyl perchlorate (4.181 gms., 0.012 moles.) in acetic acid (200 ml.). At the start of the addition, the colour of the boiling mixture instantly became yellowish green, and it turned deep turquoise by the time the addition was complete.

After the solution had cooled to room temperature, a dark violet powder was filtered off and washed with ether. This was dried in vacuo overnight, then mixed into a slurry with hot water, filtered, and washed several times alternately with hot water and ether. This left 619 mgs. of a violet powder which gradually decomposed over an indefinite range of temperature.

λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 651 (4.54). (See Plate XX).

After recrystallisation from acetonitrile, the extinction coefficient was reduced (to 4.51) and the whole curve broadened.

Note: The theoretical yield of 1-(3-methylazulen-1-yl)-methylene-3-methylazulenium perchlorate from the 1-methylazulene used is 557 mgs.

The mother liquor from the above reaction was diluted with light petrol to 1 litre, and a further crop (332 mgs.) of violet powder filtered off. The filtrate was washed with water, and the last traces of dye-salt removed by filtration through a cotton-wool plug.

The resulting solution was practically colourless, and was extracted with Conc. HCl. No azulenic material was present in the acid extracts.

CVIII 2 Guaiazulene with Triphenylmethyl Perchlorate

(i) Isolation of Triphenylmethane

Guaiazulene (2.31 gms., 0.012 moles.) was added dropwise to a boiling solution of triphenylmethyl perchlorate (724 mgs., 0.0021 moles) in acetic acid (30 ml.). The mixture was refluxed for 5 minutes, then cooled and filtered, yielding 3-(4-methyl-7-isopropylazulen-1-yl)methyleneguaiazulenium perchlorate (255 mgs., 25%) as green needles. After recrystallisation from acetic acid it had m.p. 260-262.5° (block preheated to 250°).

Found; C 73.2 H 6.7 Cl 7.4,

$C_{30}H_{33}ClO_4$ requires 73.1 6.8 7.2%

λ max. acetic acid 632 (5.03).

The mother liquor from the above reaction was poured into ether (1 litre). A further crop (241 mgs., 23%) of the dye-salt was filtered off; after recrystallisation from acetic acid it was identical in its properties with the first product. The total yield of the dye-salt was thus 496 mgs. (48%).

The ether filtrate was concentrated to low volume and the residue dissolved in benzene (500 ml.). The benzene solution, after washing with water, was extracted with conc. HCl., until the extracts were colourless (see below). It was then washed with water until free from blue water-soluble material, and extracted with conc. sulphuric acid (4 x 150 ml.)

(see below), and was then colourless. Washing was continued with sodium carbonate solution, and water, and the solvent was evaporated from the dried (Na_2SO_4) solution. The residue, in a little light petrol, was passed through a column (2.4 x 10 cm.) using light petrol as solvent and eluant. After evaporation of the colourless eluates, the residue was crystallised from ethanol. Triphenylmethane (282 mgs., 55%) was obtained as colourless needles. M.p. and mixed m.p. with an authentic sample, 92-93°. A further 82 mgs. (16%) was obtained by concentration of the ethanolic mother liquor.

The conc. hydrochloric acid extracts, after being washed with light petrol, were diluted to 3 litres with water, partially neutralised with KOH solution, and extracted with ether. The ether solution (500 ml.) was washed with sodium carbonate solution followed by water, dried (Na_2SO_4), and the solvent evaporated. The residue was chromatographed on a column (2.5 x 10 cm.), using light petrol as solvent and eluant. The blue eluates yielded 1649 mgs. of blue oil.

The conc. sulphuric acid extracts (light brown) were diluted with water to 3 litres, after being washed with benzene, and were extracted with ether. After being worked up in the usual way the extracts yielded 77 mgs. of a practically colourless oil (impure triphenylcarbinol?).

(ii) <u>Analysis of Hydrocarbons present in the Mother Liquor</u>

The preceding reaction was repeated using a mixture of guaiazulene (495 mgs., 0.0025 moles.), triphenylmethyl perchlorate (170 mgs., 0.0005 moles), and acetic acid (10 ml.). The dye-salt (55 mgs., 22%) was obtained as dark needles. The same working up procedure was followed except that light petrol was used to dilute the mother liquors, and a further 25% of the dye-salt precipitated at this stage. The light petrol solution was then extracted with conc. hydrochloric acid, and the extracts were worked up as described in the foregoing experiment, yielding 344 mgs. of blue oil. Analysis by gas-chromatography showed this to consist of guaiazulene (98%), and an unknown component (2%) (retention time 17 minutes at 200°), possibly 4-methyl-7-isopropylazulene.

CVIII 3 Guaiazulene with Tri-p-chlorophenylmethyl Perchlorate

Guaiazulene (1.803 gms., 0.0091 moles) was run into a boiling solution of tri-p-chlorophenylmethyl perchlorate (901 mgs., 0.002 moles) in acetic acid (25 ml.), the solution turning deep blue. After the solution had been refluxed for 3 minutes, about 1 ml. of the solvent was distilled off and the mixture allowed to cool to room temperature. 3-(4-Methyl--7-isopropylazulen-1-yl)methyleneguaiazulenium perchlorate (128 mgs., 12%) was filtered off and recrystallised twice from acetic acid. It softened over the range 218-223°, and gradually decomposed thereafter.

For analysis, see (CVIII 7).

CVIII 4 Guaiazulene with Tri-p-chlorophenylcarbinol in the Presence of Perchloric Acid

A mixture of guaiazulene (1.8 gms., 0.009 moles), tri--p-chlorophenylcarbinol (920 mgs., 0.0025 moles), acetic anhydride (5 ml.) and acetic acid (10 ml.) was treated with perchloric acid (0.5 ml.). After the solution had stood at room temperature overnight, 3-(4-methyl-7-isopropylazulen-1--yl)methyleneguaiazulenium perchlorate (38 mgs., 3%) was filtered off, and recrystallised from acetic acid. M.p. 252-254°(d). For analysis see (CVIII 7).

CVIII 5 Guaiazulene with p-Methoxyphenyldiphenylcarbinol in the Presence of Perchloric Acid

A mixture of guaiazulene (1917 mgs., 0.0097 moles.), p-methoxyphenyldiphenylcarbinol (520 mgs., 0.0018 moles), and acetic acid (20 ml.) was treated with perchloric acid (1 ml.). After standing for 4 hours at room temperature, 3-(4-methyl--7-isopropylazulen-1-yl)methyleneguaiazulenium perchlorate (67 mgs., 7.6%) was isolated as dark blue needles. After recrystallisation from acetic acid it decomposed over an indefinite range. For analysis, see (CVIII 7).

CVIII 6 Guaiazulene with p-Methoxyphenyldiphenylmethyl Chloride and Silver Perchlorate

A solution of silver perchlorate (576 mgs.) in acetonitrile (3 ml.) was added to a suspension of p-methoxy-phenyldiphenylmethyl chloride (781 mgs., 0.0025 moles) and

guaiazulene (518 mgs., 0.0026 moles.) in acetonitrile (3 ml.). The mixture was shaken vigorously, heated to the boiling point, and the precipitate of silver chloride was filtered off. The dark green solution was allowed to stand overnight before filtration of 3-(4-methyl-7-isopropylazulen-1-yl)-methyleneguaiazulenium perchlorate (21 mgs., 1.7%); dark blue needles, which, after recrystallisation from acetic acid, gradually decomposed > 250°.

For analysis, see (CVIII 7).

CVIII 7 Guaiazulene with Tri-p-methoxyphenylmethyl Perchlorate

A solution of guaiazulene (1230 mgs., 0.0062 moles) in acetic acid (40 ml.) was added dropwise to a boiling solution of tri-p-methoxyphenylmethyl perchlorate (259 mgs., 0.006 moles) in acetic acid (20 ml.). The deep blue solution was refluxed for 35 minutes, then allowed to cool to room temperature and stand overnight. 3-(4-Methyl-7-isopropyl-azulen-1-yl)methyleneguaiazulenium perchlorate (56 mgs., 19%) crystallised as dark blue needles. It gradually decomposed above 250° after recrystallisation from acetic acid.

For analysis see below.

The mother liquor from the above reaction was poured into ether (1½ litres) and a further quantity of the dye-salt filtered off. The filtrate was then concentrated to small volume and diluted with benzene (500 ml.). The benzene solution, after being washed with water, was extracted with

conc. HCl., until the acid extracts were colourless. After being washed free of blue water-soluble material, the benzene layer was then washed with conc. sulphuric acid (the washings were only faintly coloured) followed by water, sodium carbonate solution, and water. The dried (Na_2SO_4) solution was concentrated and the residue chromatographed as a column (2.4 x 10 cm.) using light petrol as solvent and eluant. The colourless eluates yielded trianisylmethane (34 mgs., 17%) on concentration of the solution. M.p. and mixed m.p. with an authentic sample, 62-63°.

The hydrochloric acid extracts were diluted to 3 litres with water, extracted with ether, and the extracts worked up in the usual manner. A blue oil (1030 mgs., 84% (w/w)) was obtained. Analysis results for Expts. CVIII 2 to CVIII 7 inclusive were as follows:-

For Product from Guaiazulene with

(CVIII 2)	Triphenylmethyl perchlorate	Found; C 73.2	H 6.7	Cl 7.4
(CVIII 3)	Tri-p-chlorophenylmethyl perchlorate	-	-	7.9
(CVIII 4)	Tri-p-chlorophenylcarbinol and perchloric acid	72.6	6.7	10.9
(CVIII 5)	p-Methoxyphenyldiphenylcarbinol and perchloric acid	73.4	6.8	8.6
(CVIII 7)	Tri-p-methoxyphenylmethyl perchlorate	72.3	6.7	7.7
	$C_{30}H_{33}ClO_4$ requires	73.1	6.8	7.2%

CVIII 8 1,2-Dimethylazulene with Triphenylmethyl Perchlorate

A solution of 1,2-dimethylazulene (97 mgs., 0.00062 moles), in acetic acid (2 ml.) was added to a boiling solution of triphenylmethyl perchlorate (41 mgs., 0.00012 moles) in acetic acid (8 ml.). The mixture was refluxed for three minutes, during which time it turned dark greenish-blue. It was then allowed to stand overnight, and a small quantity (3 mgs.) of solid material was filtered off. The filtrate was diluted with ether and again filtered. The residues were washed alternately with water and ether, and dried at 110° for 10 minutes. Both residues showed a fairly sharp absorption max. (acetic acid) at 667 mμ. (log ε undetermined).

The ether solution (100 ml.) was diluted with benzene (400 ml.) and extracted with syrupy phosphoric acid after being washed with water. The remaining benzene solution was then washed successively with water, sodium carbonate solution, and water, and dried (Na_2SO_4) before evaporation of the solvent. The residue was chromatographed on a column (2.5 x 10 cm.), using light petrol as solvent and eluant. Concentration of the eluates to 1 ml. yielded triphenylmethane (29 mgs., 100%), m.p. and mixed m.p. 93-94°.

The phosphoric acid extracts were diluted with water, then extracted with ether, and the extracts were worked up in

the usual way, yielding 77 mgs. of blue oil.

CVIII 9 1-Ethyl-4,6,8-trimethylazulene with Triphenylmethyl Perchlorate

A mixture of 1-ethyl-4,6,8-trimethylazulene (250 mgs., 0.00126 moles), triphenylmethyl perchlorate (432 mgs., 0.00126 moles.) and acetic acid (15 ml.), refluxed for 1 minute, changed from blue to yellow. On cooling, tarry material separated, and addition of ether (400 ml.) caused precipitation of a yellow-green powder (182 mgs.), thought to be impure 1-ethylidene-4,6,8-trimethylazulenium perchlorate, but it decomposed rapidly and could not be purified, owing to its instability.

The mother liquor was concentrated, after being washed with water, and the residue was dissolved in benzene. The benzene solution was washed successively with conc. sulphuric acid, water, sodium hydrogen carbonate solution, and water. After removal of the solvent from the dried (Na_2SO_4) solution, the residue was chromatographed on a column (2.5 x 3 cm.) using light petrol as solvent eluant. Concentration of the eluates yielded triphenylmethane (299 mgs., 97%) as colourless needles, m.p. 93-94°.

Note: This reaction was repeated under the same conditions, but using acetonitrile as solvent, and refluxing for 30 minutes, but with no improvement in results.

CVIII 10 4,8-Dimethyl-6-methoxyazulene with Triphenylmethyl Perchlorate

A mixture of 4,8-dimethyl-6-methoxyazulene (93 mgs., 0.0005 moles), triphenylmethyl perchlorate (343 mgs., 0.001 moles), and acetic acid (10 ml.), refluxed for five minutes, turned yellow. The mixture was then poured into water (100 ml.) and extracted with ether. The extracts were worked up in the usual way, and, after removal of solvent, the residue was adsorbed into a column (2.5 x 10 cm.) from the minimum volume of benzene. Elution was with benzene-light petrol (1:1). After concentrating the red eluates, the residue was treated with a solution of picric acid in ethanol, but no complex could be isolated. The mixture was then diluted with ether, and the solution was washed with sodium carbonate solution and water before drying (Na_2SO_4) and concentrating to 10 ml. Ruby-red granular crystals (88 mgs.) formed overnight. These had m.p. 223-227°(d) with softening > 211°. λ max. (benzene) 505 (broad) (2.61 for a monosubstituted product).

CIX Action of Conc. Hydrochloric Acid on 1,1'-Azulenyl-methyleneazulenium Perchlorates, and on 1-Formylazulene

CIX 1 Action of Conc. Hydrochloric Acid on 1,1'-Azulenylmethyleneazulenium Perchlorate

The salt (84 mgs.) was dissolved in conc. HCl (50 ml.), and the purple solution was refluxed for 3½ hours, after which

it was diluted with water to 1 litre and washed with light petrol. After washing the light petrol extracts with water and filtering them through a cotton-wool plug, they were quite colourless and yielded no product. The purple mother liquor was then treated with 60% perchloric acid (10 ml.) which caused a dark flocculent precipitate to form. The mixture was concentrated to 50 ml. by vacuum distillation on a water bath, and the solid (25 mgs., 30%) filtered off, washed with water and ether, and dried in vacuo.

λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 618 (5.06).

CIX 2 Action of Conc. Hydrochloric Acid on 1-(3-Methylazulen-1-yl)methylene-3-methylazulenium Perchlorate

The salt (55 mgs.) was dissolved in conc. HCl (50 ml.) and the purple solution was treated in the same way as described for the preceding experiment. Again, no neutral product was obtained, and 1-(3-methylazulen-1-yl)methylene--3-methylazulenium perchlorate (11 mgs., 20%) was recovered from the mother liquor.

λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 651 (5.03).

CIX 3 Action of Conc. Hydrochloric Acid on 3-(4-Methyl-7--isopropylazulen-1-yl)methyleneguaiazulenium Perchlorate

The salt, obtained by the reaction of triphenylmethyl

perchlorate with an excess of guaiazulene (CVIII 2) (81 mgs.) was refluxed for 3 hours, with conc. HCl. (25 ml.). It was very sparingly soluble, giving a deep purple-violet solution, which appeared to be unchanged at the end of the experiment. After cooling and filtration of the mixture, 3-(4-methyl--7-isopropylazulen-1-yl)methyleneguaiazulenium perchlorate (70 mgs., 86%) was recovered, washed with water and ether, and dried in vacuo.

λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 631 (5.06).

No neutral azulenic material was present in the mother liquor.

CIX 4 Action of Conc. Hydrochloric Acid on 3,3'-Guaiazulenylmethyleneguaiazulenium Perchlorate

The salt (52 mgs.) was refluxed with conc. HCl. (30 ml.), and after one hour, a further 20 ml. of acid was added to the deep blue solution. After being boiled for a total of 2½ hours, the solution became light green. It was cooled, poured into water (1 litre), and the mixture extracted with light petrol. The combined light petrol extracts were washed with water and extracted with conc. HCl until the light petrol solution was colourless. After being washed twice with light petrol, the acid solution was diluted with water and extracted with a further quantity of light petrol. This light petrol solution was washed with

water until free of acid, dried (Na_2SO_4) and concentrated to small volume before being filtered through a column (2.8 x 5 cm.), using light petrol as both solvent and eluant. The solvent was removed from the blue eluates by evaporation through a short Vigreux column, which left guaiazulene (28 mgs., 70%) alone, as demonstrated by gas-chromatographic analysis.

CIX 5 Action of Conc. Hydrochloric Acid on 1-(4,6,8-Trimethylazulen-1-yl)methylene-4,6,8-trimethylazulenium Perchlorate

The salt (12 mgs.) was refluxed with conc HCl (10 ml.). After 1½ hours, the violet-purple suspension had become dull green, and was poured into water (50 ml.) and extracted with light petrol. The greenish-red extracts were washed free of acid by water, dried (Na_2SO_4), and the solvent evaporated through a short Vigreux column. The residue was chromatographed on a column (2.5 x 3 cm.) using light petrol as solvent and eluant, and yielded 4,6,8-trimethylazulene (3 mgs., 41%) alone, identified by gas-chromatographic analysis.

CIX 6 Action of Conc. Hydrochloric Acid on 1-(Guaiazulen-3-yl)methyleneazulenium Perchlorate

The salt (200 mgs.) was dissolved in conc. HCl (100 ml.) and the deep purple solution refluxed for 2½ hours, during which time the colour became more violet. After cooling, the mixture was diluted with an equal volume of water and

shaken with ether (50 ml.) and perchloric acid (2 drops). A small quantity of rather tarry solid was filtered off and washed with ether. This showed a sharp absorption maximum at 618 mμ.

The mother liquor was diluted with water to 1 litre, and exhaustively extracted with ether. The aqueous phase was filtered through a cotton-wool plug, and treated with 60% perchloric acid (50 ml.). This produced a dark brown flocculent precipitate which was filtered off and recrystallised from acetonitrile, giving 20 mgs. of salt, which showed absorption maxima (acetic acid) at 633 and 638 mμ.

The ether extracts were washed with water until free of acid, dried (Na_2SO_4) and the solvent evaporated from the green solution. The residue was chromatographed on a column (2.5 x 4 cm.) using light petrol as solvent and eluant. A weak yellow band of unidentified material was subsequently eluted with benzene. After removing the solvent through a short Vigreux column, a blue oil (84 mgs.) was obtained from the light petrol eluates. Analysis by gas-chromatography showed it to consist of guaiazulene (97%) and azulene (3%).

CIX 7 <u>Action of Conc. HCl on 3-(3-Methylazulen-1-yl) methylene/guaiazulenium Perchlorate</u>

The salt (126 mgs.) was dissolved in conc. HCl (60 ml.) and the purple solution refluxed for 2½ hours, with no apparent colour change. The mixture was then cooled, poured

into water (1 litre) and exhaustively extracted with light petrol. The purple aqueous solution was washed twice with ether, filtered, and concentrated by vacuum distillation on a water bath. When the volume had been reduced to 700 ml., perchloric acid (4 ml.) was added, and the suspension further concentrated to 50 ml. Filtration yielded a green powder (49 mgs.) which was washed with water and ether, and dried in vacuo.

λ max. (acetic acid containing 0.4% (v/v) acetonitrile) 657 (4.93).

The light petrol extracts were washed with water until free of acid, and dried (Na_2SO_4), before being concentrated to small volume. The residue was chromatographed on a column (2.8 x 3 cm.) using light petrol as solvent and eluant. After evaporation of the solvent through a short Vigreux column, a blue oil (29 mgs.) was obtained. Analysis by gas--chromatography showed it to consist of guaiazulene (82%) and 1-methylazulene (18%).

CIX 8 Action of Conc. Hydrochloric Acid on 1-Formylazulene

1-Formylazulene (320 mgs.) was dissolved in conc. HCl (25 ml.) and the solution refluxed for 2 hours. Initially the solution was yellow, but it became purple after a few minutes. After refluxing, the mixture was poured into water (800 ml.) and washed several times with ether; the ether washings were quite colourless. After filtration, the purple

solution was concentrated to 50 ml. by vacuum distillation on a water bath, and treated with perchloric acid (5 ml.). 1,1'-Azulenylmethyleneazulenium perchlorate (124 mgs., 33%) was filtered off as a green powder, washed with water and ether, and dried in vacuo.

λmax. (acetic acid containing 0.8% (v/v) acetonitrile) 618 (5.08).

CX Reactions of Azulenes with 1,1'-Azulenylmethylene-azulenium Perchlorates

General Method

The azulene and the dye-salt, in a molar ratio of approximately 3:1, were heated together in the solvent. At the end of the reflux time, the mixture was cooled and filtered. After washing it with ether, and drying in vacuo, the visible spectrum was determined for the crude recovered salt.

The mother liquors were diluted with light petrol (100 - 200 ml.) and filtered or decanted if necessary. The solution was then washed with water until free from acid, dried (Na_2SO_4), and, after being concentrated to a small volume, was chromatographed, using light petrol as solvent and eluant. The solvent was evaporated from the eluates using a short Vigreux column for the last 25 ml., and the residual oil was examined by gas-chromatography.

CX 1 <u>1-Methylazulene with 1-(3-Methylazulen-1-yl)methylene-azulenium Perchlorate</u>

(i) The salt (39 mgs., 0.000102 moles) and 1-methylazulene (45 mgs., 0.000317 moles) were mixed with acetic acid (10 ml.), and the suspension refluxed for 15 minutes. After the mixture had been worked up according to the general procedure described above, the dye salt (31 mgs., 79% (w/w)) was recovered and examined spectrophotometrically. λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 635 (The spectrum shows broadening on the long wavelength side, relative to the starting material).

Analysis of the blue hydrocarbon recovered (37 mgs.), showed it to be a mixture of 1-methylazulene (95%), azulene (4%), and an unidentified product (1%) with small retention time (1 minute at 150°).

(ii) A mixture of the salt (42 mgs., 0.00011 moles), 1-methylazulene (55 mgs., 0.000387 moles) and acetonitrile (10 ml.) was refluxed for 1 hour, and then worked up in the prescribed manner.

<u>Recovered Salt</u> (24 mgs.): λmax. (acetic acid containing 0.8% v/v acetonitrile) 635 (5.05).

<u>Recovered Hydrocarbon</u> (33 mgs.): consisted of 1-methylazulene (95%) and azulene (5%).

(iii) A mixture of the salt (25 mgs., 0.000066 moles), 1-methylazulene (31 mgs., 0.000218 moles) in acetic acid

(15 ml.), was refluxed for 2 hours, then worked up in the usual manner.

Recovered Salt (24 mgs.): λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 635 (4.99).

Recovered Hydrocarbon (19 mgs.): consisted of 1-methylazulene (86%) and azulene (14%).

GX 2 Guaiazulene with 1,1'-Azulenylmethyleneazulenium Perchlorate

A mixture of the salt (50 mgs., 0.000136 moles) and guaiazulene (110 mgs., 0.000556 moles), in acetic acid (5 ml.), was refluxed for 1.75 hours, and worked up in the usual way.

Recovered Salt (39 mgs.): λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 618 (5.01). A trace of material was precipitated from the mother liquor by the addition of light petrol. This had λ max. (broad) at 620 mμ.

Recovered Hydrocarbon (105 mgs.): this consisted of guaiazulene (96%) and azulene (4%).

GX 3 4,6,8-Trimethylazulene with 1,1'-Azulenylmethyleneazulenium Perchlorate

A mixture of the salt (183 mgs., 0.0005 moles), 4,6,8-trimethylazulene (257 mgs., 0.00151 moles) and acetic acid (20 ml.) was refluxed for 19 hours under a stream of nitrogen, and worked up in the usual way.

Recovered Salt (167 mgs.): λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 616 (broad) (4.13).

Recovered Hydrocarbon (215 mgs.). This consisted of 4,6,8-trimethylazulene (79%) and azulene (21%).

CX 4 Guaiazulene with 1-(3-Methylazulen-1-yl)methylene--3-methylazulenium Perchlorate

A mixture of the salt (93 mgs., 0.000235 moles), guaiazulene (145 mgs., 0.000732 moles) and acetic acid (10 ml.) was refluxed for 3 hours, and worked up in the usual way.

Recovered Salt (84 mgs.): λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 651 (5.00). A small quantity of material was deposited from the mother liquor by the addition of light petrol, λ max. 642.

Recovered Hydrocarbon (136 mgs.). This consisted of guaiazulene (90%), 1-methylazulene (9%), and a trace of an unidentified product (retention time 3 minutes at 200°).

CX 5 1-Methylazulene with 1-(Guaiazulen-3-yl)methylene-azulenium Perchlorate

A mixture of the salt (107 mgs., 0.000245 moles), 1-methylazulene (132 mgs., 0.00093 moles) and acetic acid (20 ml.) was refluxed for 2 hours, and worked up in the usual way.

Recovered Salt (83 mgs.): λ max. (acetic acid containing 0.8% (v/v) acetonitrile) 647.

Recovered Hydrocarbon (130 mgs.). This consisted of azulene (15%), 1-methylazulene (40%), and guaiazulene (45%).

PART D.

DI 1-Formylazulene

This was obtained as a purple oil by reaction of azulene with dimethyl formamide and phosphorus oxychloride, as described by Treibs, Neupert, and Hiebsch[72]. Yield 71% (Lit.,[72] 94%).

DII 1-Methylazulene

The method of Treibs, Neupert, and Hiebsch[72] was modified as follows. Hydrazine hydrate (64% (w/w) (2 ml.)) was added to 1-formylazulene (1.625 gms.) dissolved in ethylene glycol (25 ml.). The mixture was heated in a 50 ml. Claisen flask to just below the boiling point, and 7 pellets of potassium hydroxide were added, one at a time. Approximately one-half of the solvent was then distilled off as rapidly as possible, or until the distillate was no longer blue.

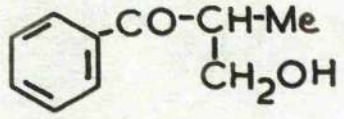
The distillates from two such runs were combined, poured into water (200 ml.) and extracted with ether. The ether solution was washed successively with dil. hydrochloric acid, sodium carbonate solution, and water, and the solvent was evaporated after the solution had been dried over Na_2SO_4. The residual oil was chromatographed on a column (2.5 x 10 cm.) using light petrol as solvent and eluent. Evaporation of solvent from the blue light petrol eluates left 1-methylazulene (1.920 gms. 65%) as a blue oil. After two distillations at 60-80°/0.1 m.m., it crystallised

as blue plates, m.p. 24-25°.

DIII 2-Methylazulene

This was prepared by the six-stage synthesis described by Plattner & Wyss[42], in which propiophenone is converted successively into intermediates, as follows.

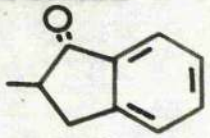
DIII 1 2-Benzoyl-n-propanol (1)



(1)

This was prepared from propiophenone and paraformaldehyde as described[210]. The yield of colourless oil was 58%, b.pt. 158-160°/C. 10 m.m. (Lit.[210] 41%, b.pt. 143-145°/5 m.m.).

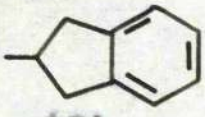
DIII 2 2-Methylindanone (2)



(2)

Cyclisation of 2-benzoyl-n-propanol was effected with conc. sulphuric acid, as described[210], yielding 2-methylindanone as a colourless oil, b.pt. 95-110°/C. 10 m.m. (74%). (Lit.[210] 67%, b.pt. 88-90°/3 m.m.).

DIII 3 2-Methylindane (3)



(3)

The Clemmensen reduction procedure, applied to 2-methylindanone, gave 2-methylindane in 60% yield, b.pt. 65-70°/10 m.m.

DIII 4 Ring Expansion of 2-Methylindane by Ethyl Diazoacetate

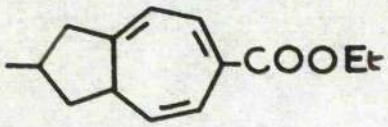
The reaction was carried out in a 250 ml. 3-neck flask, fitted with a stirrer, a dropping funnel, and an air condenser, through which was hung a thermometer. An isomantle coupled to a variable voltage transformer was found to be the most satisfactory apparatus for controlling the temperature.

Ethyl diazoacetate[235] (8 gms.) was added dropwise, with stirring, over five hours, to 2-methylindane (40 gms.). The temperature was maintained at 135° ± 2° during this time. A 50 ml. dropping funnel drawn to a capillary was used for the addition, and was adjusted to give a dropping rate of approximately 1 drop/3 seconds. Towards the end of the addition, the dropping rate was maintained by external pressure from rubber bellows.

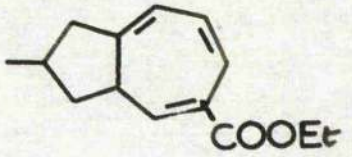
After the addition was complete, the temperature was raised to 165-170°, and kept there, with stirring, for a further 5-6 hours. The mixture was then distilled under reduced pressure, and the fraction with b.p. 60-120°/10 m.m. (b.pt. of bulk 60-65°/10 m.m.) (about 33 gms.) was recycled. The fraction with b.p. 120-150°/10 m.m. (c. 6 gms.), a dark red oil, was used directly for the next stage without further purification.

This process was repeated several times until sufficient product had been obtained. A total of 55 gms. of 2-methylindane was treated, and it yielded 30 gms. of the

crude ester(s) (4) and/or (5).

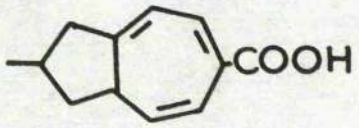


(4)

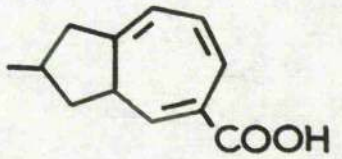


(5)

DIII 5 Hydrolysis of Crude Ester(s)



(6)



(7)

A mixture of the crude ester(s) (4) and/or (5) (30 gms.), potassium hydroxide (12 gms.), and methanol (200 ml.), was refluxed for eight hours, during which time it turned brown and deposited a considerable quantity of solid material. The mixture was then poured into water (1 litre), and washed with ether. The aqueous phase was then acidified with conc. hydrochloric acid, and extracted with ether. After being washed with water until free of acid, the ether solution was dried (Na_2SO_4), and the solvent was evaporated, leaving the acid(s) (6) and/or (7) (22 gms. 85%) as a viscous rancid smelling brown oil. This crude product was used for the next stage without further purification.

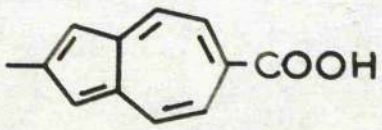
DIII 6 2-Methylazulene: Isolation

20% Palladium charcoal catalyst[211] (0.5 gms.) was added to the crude acid(s) (6) and/or (7) (5 gms.) in a 10 ml. Claisen flask, and the mixture heated over a free flame.

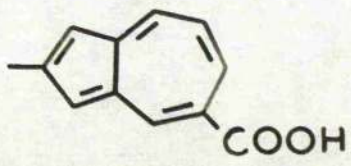
After a few minutes the colour deepened, and a violet-blue fraction distilled with b.p. C.220°. 22 Gms. of the crude acid(s) was treated in this way, and the combined distillates were dissolved in benzene (300 ml.) and extracted with 90% orthophosphoric acid. After dilution of the acid extracts with water, and extraction of the resulting solution with ether, the ether solution was washed successively with sodium carbonate solution*, and water. The solvent was evaporated from the dried (Na_2SO_4) solution, and the residual blue oil (2.6 gms.) was chromatographed on a column (5 x 20 cm.), using light petrol as solvent and eluant. The blue eluates yielded 2-methylazulene (1.03 gms., 6.3%, Lit.[42] 8%) as blue plates which had m.p. 40-43° (Lit.[42] 47-48°). The picric acid complex was prepared, and after one recrystallisation from ethanol it had m.p. 129-131° (Lit.[42] 130-131°).

λ max. (petrol)	674	613	569	561
λ max. (Lit.)[42] (pentane)	676	613	570	561

Note: The blue sodium carbonate washings* were acidified. The mixture was extracted with ether, and the ether solution was worked up in the usual way, yielding a dark blue oil (843 mgs.). This may be 2-methylazulene-6-carboxylic acid (8) and/or the isomer (9). There is no report of a similar observation in Plattner & Fyss's description of this synthesis[42].



(8)



(9)

DIV 1,2-Dimethylazulene

A mixture of 1-formyl-2-methylazulene (CV 3) (142 mgs.), ethylene glycol (5 ml.), and hydrazine hydrate (64% (w/w) (1 ml.)) was heated to just below the boiling point in a 10 ml. Claisen flask. Three crushed pellets of KOH were added portionwise and the mixture was distilled as rapidly as possible until the distillates were no longer blue. The combined distillates from two such runs were dissolved in light petrol (400 ml.), and the resulting solution was washed successively with conc. hydrochloric acid-water (1:3), water, sodium carbonate solution, and water. The solution was dried (Na_2SO_4), concentrated to small volume, and adsorbed onto a column (2.5 x 15 cm.). Concentration of the blue light petrol eluates left 1,2-dimethylazulene (184 mgs., 71%) as blue plates, m.p. 48-50° (Lit.[42] 58-59°). The sym--trinitrobenzene complex had m.p. 158-160° (Lit.[42] 166-167°).

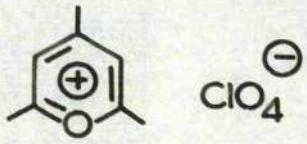
λ max. (petrol)	715	685	646	625	591
λ max. Lit.[42] (hexane)	720	683	648	625	591

Note: The melting points of both 2-methylazulene and 1,2-dimethylazulene were found to be lower than those previously reported[42]. They were, however, sharp, and spectral data were in good agreement with those recorded in the literature, so that there was no reason to suspect that the present products were impure.

DV 4,6,8-Trimethylazulene

The method of Hafner & Kaiser[56] using the reaction between sodium cyclopentadienide and 2,4,6-trimethylpyrylium perchlorate was modified as follows.

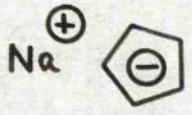
DV 1 2,4,6-Trimethylpyrylium Perchlorate (10)



(10)

Following the method of Diels and Alder[212], an ice-cold solution of perchloric acid (30 gms.) in acetic anhydride (60 gms.) was carefully added to an ice-cold solution of mesityl oxide (30 gms.) in acetic anhydride (40 gms.). After the addition was complete, the mixture was warmed on a water-bath at 50° for 20 minutes. 2,4,6-Trimethylpyrylium perchlorate (10) (29 gms., 86%) crystallised as a white powder, and was filtered from the cooled mixture, washed successively with acetic acid, ethanol, and ether, and dried in vacuo. The product was used for the next stage without further purification. M.p. 246.5-247.5°(d). (Lit.[213] 242°(d), 41% yield after further purification[212]).

DV 2 Sodium Cyclopentadienide (11)



(11)

The calculated quantity of clean sodium was converted to a sand (see below, note 2). After being washed with tetrahydrofuran, it was rapidly rinsed into a 250 ml. 3-neck flask with about 100 ml. tetrahydrofuran. Freshly distilled cyclopentadiene was then added dropwise, with stirring, under a stream of nitrogen, until all the sodium had dissolved. The temperature was kept between 0 and 5°.

DV 3 Potassium Tert. Butoxide

An approximately 1 molar solution of this was prepared by adding 49 gms. potassium in 1 c.c. lumps to 1 litre of dry tert. butanol, and allowing it to stand until it had all dissolved.

DV 4 Condensation of 2,4,6-Trimethylpyrylium Perchlorate with Sodium Cyclopentadienide

A solution of sodium cyclopentadienide (11), prepared from 8.1 gms. sodium, in tetrahydrofuran (100 ml.), was added dropwise to a vigorously stirred suspension of 2,4,6-trimethylpyrylium perchlorate (10) (78 gms.) in tetrahydrofuran (300 ml.), under a stream of nitrogen in a 2-litre 3-neck flask. The temperature was kept below -20° by means of a solid CO_2-acetone bath. A purple colour was produced momentarily with each drop, which subsequently turned blue, and then colourless, until about half-way through the addition, when the whole mixture became purple. When the addition was complete, the mixture was allowed to stand in a

refrigerator at 0°C overnight, then 1 litre 1M potassium tert. butoxide in tert. butanol was added in portions, and the whole mixture immediately steam distilled. 4,6,8-Trimethylazulene distilled as a purple oil, and in the latter stages it crystallised spontaneously in the water. When the steam distillation was complete, the solid product was filtered off and crystallised from ethanol. The filtrates were extracted with benzene, and after washing the solution, it was extracted with conc. HCl. These acid extracts were washed with benzene, diluted with water and extracted with ether. The ether solution was worked up in the usual way, and after evaporation of the solvent, the residue was chromatographed on a column (4 x 30 cm.), using light petrol as solvent and eluant. The residue obtained after evaporation of the purple eluates was combined with the product filtered from the later steam distillates, and crystallised from ethanol. This yielded 4,6,8-trimethylazulene (57.5 gms., 96%) (Lit.[56] 62%) as purple plates m.p. 76-77° (Lit.[56] 81-82°).

Note 1: Although Hafner & Kaiser[56] quote the m.p. of 4,6,8-trimethylazulene as 81-82°, in the present work it was never found possible to obtain a higher m.p. than 76-77°.

Note 2: Sodium Sand: The most satisfactory method of preparation was to heat the clean sodium metal under dry toluene (C. 10 ml./gm. of sodium), in a suitable size bolt-

-neck flask, on an isomantle heater. When the sodium had just melted, the flask was stoppered firmly with a rubber bung, then wrapped in a cloth and shaken vigorously for several seconds. The toluene was then decanted off, and the sodium sand washed with tetrahydrofuran.

Note 3. Solvents: The toluene was purified by refluxing for two days over sodium wire, followed by distillation.

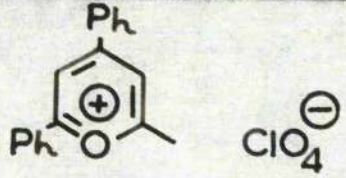
tert. Butanol was dried by refluxing over calcium hydride for two-three hours, and then distilling it through a Vigreux column.

Tetrahydrofuran was treated as described in the notes prefacing Part C.

Note 4: Nitrogen for this work was purified by passing it through a series of eight traps. These were as follows: (1) mercury pressure blow off; (2), and (3), conc. sulphuric acid; (4), (5), and (6), alkaline pyrogallol solution (15 gms. pyrogallol in 100 ml. 50% (w/w) aqueous sodium hydroxide solution); (7), loosely packed glass wool; (8), empty.

DVI 4,6-Diphenyl-8-methylazulene[56]

DV 1 2,4-Diphenyl-6-methylpyrylium Perchlorate (12)[212]



(12)

Freshly distilled acetophenone (155 gms.) was added in portions to a mixture of perchloric acid (78 ml.) and acetic

anhydride (400 ml.), cooled in an ice/salt bath. After a few minutes the solution turned dark green. A small portion of the solution was withdrawn and treated with ether. The precipitated material was then used to seed the remaining reaction mixture, and after 10 minutes the product (12) (114 gms. 51%) was filtered off, washed successively with acetic acid, ethanol, and ether, and dried in vacuo. M.p. 203-206°(d) (Lit.[214] 204°(d), yield[212] 54%).

DVI 2 Condensation of 2,4-Diphenyl-6-methylpyrylium Perchlorate with Sodium Cyclopentadienide

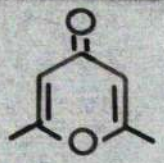
The apparatus and procedure was the same as that described in preparation (DV 4). A solution of sodium cyclopentadienide (from 10 gms. sodium) in tetrahydrofuran (200 ml.) was added to the pyrylium salt (12) in tetrahydrofuran (100 ml.).

After completion of the addition, the mixture was allowed to warm up to room temperature, whereupon a solution of potassium tert. butoxide in tertiary butanol (1M., 400 ml.) was added, and the mixture was extracted with ether. The ether solution was worked up in the usual way, and after removal of the solvent, the dark green residue was adsorbed onto a column (4 x 30 cm.) from the minimum volume of benzene. Evaporation of the blue light petrol eluates left 4,6-diphenyl--8-methylazulene (8.06 gms. 19%, Lit.[56] 25%) as a deep blue glass-like mass which did not crystallise. This material was

distilled under reduced pressure before use.

DVII 4,8-Dimethyl-6-Methoxyazulene[56]

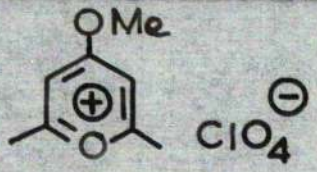
DVII 1 2,6-Dimethyl-γ-Pyrone (13)



(13)

This preparation is based on that described by Arndt & Eistert[215]. Dehydroacetic acid (140 gms.) was heated with conc. hydrochloric acid (400 ml.) until foaming ceased. The mixture was then concentrated to low volume under reduced pressure, and, after cooling, the solid material was filtered off and washed with water. After two recrystallisations from pyridine, 2,6-dimethyl-γ-pyrone (13) (45 gms., 44%) was obtained as white needles, m.p. 132-133° (Lit. 132°, yield 60%)[215].

DVII 2 2,6-Dimethyl-4-methoxypyrylium Perchlorate (14)



(14)

This preparation follows that described by Baeyer[216]. 2,6-Dimethyl-γ-pyrone (13) (45 gms.) was stirred with dimethyl-sulphate (50 ml.) on a water-bath at 60° until it had all dissolved (25 minutes). The orange syrup was cooled in an ice bath and treated with perchloric acid (150 ml., 20%

(w/w)). The product (14) crystallised at once as orange needles, and, after 30 minutes, it was filtered off, washed successively with water, acetone, and ether, and dried in vacuo. Yield 53 gms., (61%) (Lit.[216] 47%).

DVII 3 Condensation of 2,6-Dimethyl-6-methoxypyrylium Perchlorate with Sodium Cyclopentadienide

The apparatus and procedure was the same as for preparation (DIV 4). 2,6-Dimethyl-4-methoxypyrylium perchlorate (14) (50 gms.) was treated with a solution of sodium cyclopentadienide prepared from 5 gms. sodium.

After completion of the addition, the brownish-red mixture was treated with a 1-M. solution of potassium tert. butoxide in tert. butanol (500 ml.), and was then refluxed for 40 minutes, during which time it turned crimson and then brown. The cooled mixture was diluted with water, and extracted with ether, and the ether solution was worked up in the usual way. The residue obtained after evaporation of the solvent was dissolved in the minimum volume of benzene, and adsorbed onto a column (4 x 25 cm.). The scarlet light petrol benzene (1:1) eluates were extracted with 60% sulphuric acid. The acid solution was washed with light petrol, diluted with water and extracted with ether. The ether solution was worked up in the usual way. After removal of the solvent, the residue was adsorbed onto a column (4 x 20 cm.) from the minimum volume of benzene. Elution

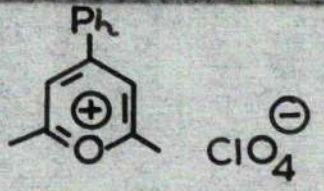
with light petrol benzene (1:1) yielded 4,8-dimethyl-6--methoxyazulene (8.8 gms., 23%) (Lit.,[56] 55%) as crimson needles, m.p. 100-101° (Lit.,[56] 100-101°).

Note 1: In Hafner & Kaiser's paper[56] it is stated that the reaction mixture was worked up by the shorter procedure of diluting with petrol, and extracting this petrol solution with 60% sulphuric acid. In the present instance, however, all attempts to follow this were frustrated by the formation of an intractable emulsion.

Note 2: The acid extraction must be carried out fairly rapidly in order to avoid some decomposition.

DVIII 4,8-Dimethyl-6-phenylazulene[56]

DVIII 1 2,6-Dimethyl-4-phenylpyrylium Perchlorate (15)



(15)

This was prepared by the method of Baeyer and Piccard[217]. A Grignard reagent was prepared in the usual way from bromobenzene (40 gms.) in ether (100 ml.). This was cooled in an ice-salt bath and to it was added a mixture of 2,6-dimethyl-γ-pyrone (13) (40 gms.), ether (500 ml.) and anisole (100 ml.), over 10 minutes, with stirring. The crimson mixture was stirred for three hours before the addition of perchloric acid (500 ml., 20% (w/w)). After

being allowed to stand overnight, the product (15) (35 gms., 38%) was filtered off as pale brown needles, washed successively with ethanol and ether, and dried in vacuo. M.p. 208-211°(d) (Lit., 210-212°(d), yield 35%)[217].

DVIII 2 Condensation of 4,8-Dimethyl-6-phenylpyrylium Perchlorate with Sodium Cyclopentadienide

The apparatus and procedure was the same as in (DV 4). A solution of sodium cyclopentadienide, prepared from 7 gms. sodium in tetrahydrofuran (100 ml.) was added to the pyrylium salt (15) (35 gms.) in tetrahydrofuran (200 ml.) as described (DV 4).

After the addition was complete, the mixture was allowed to warm up to room temperature, and was then diluted with benzene (800 ml.) and extracted with 90% orthophosphoric acid (5 x 400 ml.). The acid extracts were diluted to 5 litres with water before being extracted with ether. The ether solution was worked up in the usual way. After removal of the solvent, the residue was chromatographed on a column (4 x 20 cm.). Evaporation of the blue light petrol eluates left 4,8-dimethyl-6-phenylazulene (14 gms., 47%) as blue needles, m.p. 96-99° (Lit. 100-101°, yield 87%)[56].

This product was purified before use by a further extraction with 60% (w/w) sulphuric acid from a benzene solution, with the usual working up procedure. M.p. was then 100-101°,

after crystallisation from light petrol.

Note: Considerable losses by decomposition occur during the acid extraction, but this appears to be the most satisfactory way of obtaining a pure product.

DIX 1-Ethyl-4,6,8-trimethylazulene

1-Ethylidene-4,6,8-trimethylazulenium perchlorate (CI 27) (852 mgs.) was added portionwise over 30 minutes to a stirred suspension of lithium aluminium hydride (400 mgs.) in ether (100 ml.), at room temperature. After completion of the addition, the violet-blue mixture was refluxed for 30 minutes, cooled, and the excess of lithium aluminium hydride was decomposed by the careful addition of water. Dilute sulphuric acid was then added to clear the aqueous layer, and the mixture subsequently extracted with ether. The ether solution was worked up in the usual way, and, after removal of the solvent, the residue was chromatographed on a column (2.5 x 8 cm.). Evaporation of the violet-blue eluates left 1-ethyl-4,6,8-trimethylazulene (433 mgs., 76%) as a blue oil. The sym-trinitrobenzene complex had m.p. 146-148° (Lit.[164] 148-149°).

DX Triphenylcarbinol ($Ph_3C.OH$)

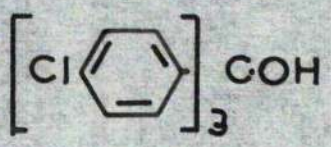
This was prepared from benzophenone, as described[218], in 87% yield, with m.p. 161-162°. (Lit. 161-162°, yield 89%)[218].

DXI Triphenylmethyl Perchlorate ($Ph_3C^+ClO_4^-$).

The basis of this method is that described by Hofmann & Kirmreuther[219] which is readily adaptable to large scale practice.

Perchloric acid (75 ml.) was added in 5 ml. portions to an ice-cold mixture of triphenylcarbinol (100 gms.), acetic anhydride (2 litres), and acetic acid (200 ml.). The temperature was kept below 15°C. Triphenylmethyl perchlorate (107 gms., 82%) crystallised at once as orange needles, and was filtered off, washed with acetic acid followed by ether, and dried in vacuo. The product decomposed >155° (Lit.,[219] m.p. 150°).

DXII Tri-p-chlorophenylcarbinol (16)



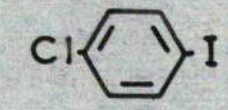
(16)

This preparation followed Baeyer's work[220], and started from p-chlorobenzoic acid, and p-chloroaniline.

DXII 1 Ethyl-p-chlorobenzoate

This ester was prepared from p-chlorobenzoic acid in 90% yield by the method described by Vogel[221]. The product was a colourless oil, b.pt. 237-238°.

DXII 2 p-Chloroiodobenzene (17)



(17)

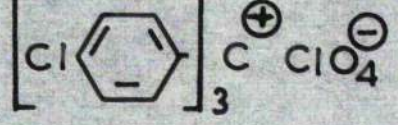
This was prepared from p-chloroaniline in 73% yield, b.pt. 104-105°/C. 15 m.m. (Lit.[220] b.pt. 100°/13 m.m.) by the method described[220].

DXII 3 Reaction of the Grignard Reagent from p-Chloroiodobenzene with Ethyl-p-chlorobenzoate

A Grignard reagent was prepared from p-chloroiodobenzene (84.3 gms.) in ether (400 ml.) in the usual way. To this was added (dropwise) a solution of ethyl-p-chlorobenzoate (27.4 gms.) in ether (300 ml.), with stirring. Reaction proceeded quietly, and on completion of the addition, the mixture was refluxed for 6 hours. Water and dilute sulphuric acid were then cautiously added to the cooled mixture until a clear solution was obtained. The ether was distilled off, and the residue steam distilled until the distillates were quite clear. The remaining yellow-brown oil was dissolved in ether and the ether solution was washed with sodium bicarbonate solution followed by water. After drying (Na_2SO_4), and removal of the solvent, the residue was heated on a water bath for 1 hour at reduced pressure, to remove traces of solvent. Subsequent crystallisation from light petrol yielded the carbinol (16) (30.5 gms., 57%) as colourless

needles, which after one recrystallisation from light petrol had m.p. 95-96° (Lit. 98-99°)[220].

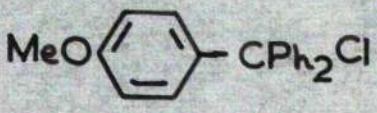
DXIII Tri-p-chlorophenylmethyl Perchlorate (18)



(18)

The method described for the preparation of triphenylmethyl perchlorate (DXI) was used. This yielded the perchlorate (18) (7.307 gms., 84%) as brown needles, which were washed with acetic acid, and dried in vacuo. M.p. 167-169° (Lit. 172-174°)[220]

DXIV p-Methoxyphenyldiphenylmethyl Chloride (19)



(19)

This preparation followed that of Burton & Cheeseman[223].

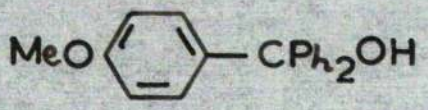
DXIV 1 Dichlorodiphenylmethane ($Ph_2C.Cl_2$)

This was prepared, by the method of Andrews & Kaeding[224], as a green oil, which yielded a colourless oil (71%) (Lit. 70%)[224] after two distillations at reduced pressure. A volumetric extinction, in the manner described, showed it to be 94% pure.

DXIV 2 Reaction of Dichlorodiphenylmethane with Anisole

A Friedel-Craft reaction between dichlorodiphenylmethane and anisole was carried out as described[223], and after the crude product had been boiled with acetyl chloride for 20 minutes, it yielded p-methoxyphenyldiphenylmethyl chloride (19) (84%) as colourless needles, m.p. 118-121.5° (lit.[223] m.p. 121-123°, yield 91%).

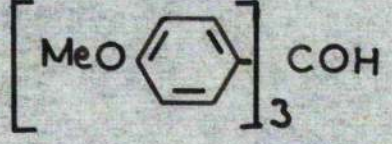
DXV p-Methoxyphenyldiphenylcarbinol (20)



(20)

p-Methoxyphenyldiphenylmethyl chloride (19) (19.56 gms.) was heated to the boiling point with 2-N sodium hydroxide solution (150 ml.). The mixture was then cooled, and extracted with ether. The ether solution was worked up in the usual manner, and, after evaporation of the solvent, the carbinol (20) (11.34 gms., 62%) was left as a pale brown oil, which crystallised from light petrol as colourless needles, m.p. 73-75°.

DXVI Tri-p-methoxyphenylcarbinol (21)

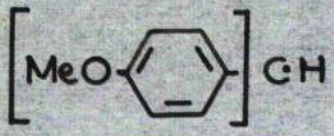


(21)

The synthesis of this carbinol (21) by the condensation of p-anisaldehyde with anisole to give tri-p-methoxyphenylmethane, followed by oxidation of the methane to (21), has been described by several workers[225,226,227].

In the present instance, trouble was experienced at the oxidation step. The described experimental procedures were therefore considerably modified.

EXVI 1 Tri-p-methoxyphenylmethane (22)



(22)

(23)

Conc. sulphuric acid (175 ml.) was carefully added to an ice-cold mixture of p-anisaldehyde (23) (90 gms.) and anisole (150 gms.) and acetic acid (500 ml.). The mixture was warmed on a water-bath to 50° and allowed to stand at room temperature for 4 hours. The dark brown mixture was then poured onto crushed ice (2 litres), and extracted with ether. The ether solution was worked up in the usual way, and the residue remaining after removal of the solvent was distilled under reduced pressure, yielding the methane (22) (46 gms., 19% based on p-anisaldehyde) as a viscous yellow oil. This crystallised from benzene light petrol 1:1) to give colourless needles, m.p. 44-46° (Lit.[225] 45-47°).

Note: A higher yield (62%) was reported in the literature[225],

but the reaction mixture was allowed to stand for several days before being worked up.

DXVI 2 Oxidation of Tri-p-methoxyphenylmethane

A mixture of the methane (22) (30 gms.), lead tetraacetate[228] (21 gms.), and acetic acid (1 litre) was refluxed for 20 minutes. The orange solution was poured into water (2 litres) and extracted with ether. The ether solution was worked up in the usual way and the solvent exchanged for benzene (500 ml.). The benzene solution was extracted several times with 77% (w/w) sulphuric acid (a total of 1200 ml.) and the acid extracts poured into water (8 litres), after being washed with benzene. The diluted acid extracts were extracted with ether, and the ether solution was worked up in the usual way. After evaporation of the solvent, the residue was adsorbed onto a column (4 x 25 cm.) from the minimum volume of benzene. The column was washed with benzene-light petrol (1:2) (2 litres), and the washings yielded a small quantity of an unidentified substance, m.p. 135-137°. Subsequent slow elution with benzene-light petrol (2:1) yielded tri-p-methoxyphenylcarbinol (21) (3.4 gms., 11%) as colourless needles, m.p. 80-82°. (Lit.[227] 80-82°).

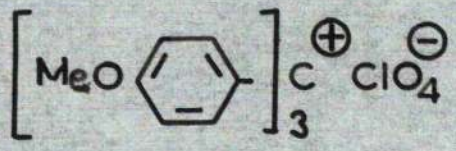
Note 1: Attempts to use lead dioxide for the oxidation, as described by Burton & Cheeseman[227], were unsuccessful. Similar results attended the use of red-lead.

Note 2: The yield of carbinol (21) reported above does not

represent the maximum that may be obtained by this procedure. The somewhat tedious elution was not continued after the required quantity of product had been obtained. The conditions described for the chromatography are critical. Elution is even slower with an eluting solvent containing less benzene than the optimum, but a higher proportion of benzene washes through an orange contaminant.

Note 3: The presence of the carbinol (21) in the eluates was detected by the yellow colour it generates, when a solution is shaken with conc. sulphuric acid.

DXVII Tri-p-methoxyphenylmethyl Perchlorate



(24)

This was prepared from the carbinol (21) in the same manner as described for the preparation of triphenylmethyl perchlorate (DXI). The product (24) was obtained as crimson needles (75%), m.p. 193-195° (Lit.[227] m.p. 193-195°, yield 89%).

DXVIII Hydroxymethyleneacetone, Sodium Salt of (25)

(25)

Claisen's method[179] was used to prepare the salt of the hydroxymethylene ketone (25) from AnalaR acetone, using

n-amylformate and sodium ethoxide. Yield 48% (Lit.[179] 46%).

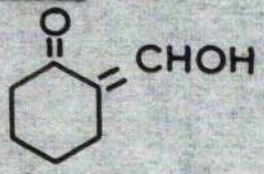
DXIX Hydroxymethyleneacetophenone, Sodium Salt of (26)

$$Ph.CO.\overset{\ominus}{C} = CHOH \quad Na^{\oplus}$$

(26)

Ethyl formate and sodium wire were used to formylate acetophenone as described by Auwers and Schmidt[229]. Yield 86% (Lit.[229] 90%).

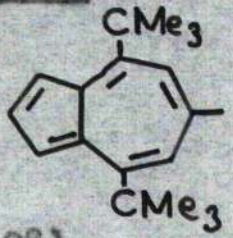
DXX 2-Formylcyclohexanone (27)



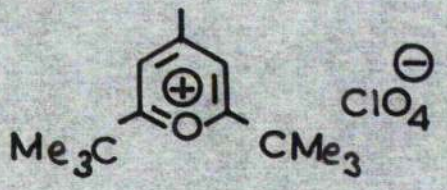
(27)

This was prepared by Borsche's method[230], from cyclohexanone, using sodium wire and amyl formate. Yield 65%, b.pt. 87-89°/C.15 m.m. (Lit.[230] 62% b.pt. 87°/14 m.m.).

DXXI 4,8-Ditertiarybutyl-6-methylazulene (28): Attempted Synthesis



(28)



(29)

The apparatus and procedure used were the same as described in (DV 4). The pyrylium salt (29) (7.9 gms.) was treated with a 1.M. solution of sodium cyclopentadienide prepared from 2 gms. of sodium in tetrahydrofuran.

After completion of the addition, the brown mixture was allowed to warm up to room temperature and was refluxed for 30 minutes. The cooled mixture was treated with 1.M. potassium tert. butoxide in tert. butanol solution (100 ml.), and then poured into water and extracted with light petrol. No azulenic material was present.

DXXII 1-Formyl-4,6,8-trimethylazulene: Attempted Wolf--Kishner Reduction

(a) The aldehyde (2 gms.) was treated in the same way as described for the reduction of 1-formylazulene (DII). When the ethylene glycol was distilled off, it was only faintly coloured, and no useful product could be isolated from the distillate or residue.

(b) The slight modification of procedure described by Hafner and Bernhard[71] was applied. The aldehyde (100 mgs.) was dissolved in ethanol (2 ml.) with hydrazine hydrate (64% w/w), (0.5 ml.)), and warmed on a water bath until it became dark violet. This solution was then added dropwise to a solution of potassium hydroxide (190 mgs.) in ethylene glycol (2 ml.) at C.190°. After completion of the addition (30 minutes), ethanol was added dropwise until the distillates were colourless. The pale blue distillate was poured into water and extracted with ether, and the ether solution was worked up in the usual way. After chromatography on a column (2.5 x 10 cm.), using light petrol as solvent and

eluant, a blue oil (12 mgs.) was obtained, presumably 1,4,6,8-tetramethylazulene, but shortage of material prevented further characterisation.

DXXIII 1-Formyl-4,8-dimethyl-6-methoxyazulene: Attempted Wolf-Kishner Reduction

The aldehyde was treated in the same way as described for the reduction of 1-formylazulene (DII), but no useful material could be isolated from the colourless distillates or the brown reaction residue.

APPENDIX.

Appendix:

Gas-liquid Chromatographic Analyses

The gas-liquid chromatograms quoted in this thesis were recorded on a Pye Argon Chromatograph, using a 4' x 4 m.m. column packed with 10% Apiezon L grease on celite. The argon flow rate was 33 ml. per minute, and detector voltage 1000 volts (β-ray ionisation detector).

For azulene/1-methylazulene mixtures, a temperature of 150° was used, the mean retention times being 15 and 27 minutes respectively. Mixtures containing 4,6,8-trimethylazulene and/or guaiazulene were run at 200°, the mean retention times being as follows: azulene 3.9 minutes, 1-methylazulene 6.3 minutes, 4,6,8-trimethylazulene 17.8 minutes, guaiazulene 21.9 minutes.

Control Experiment 1

A standard mixture of azulene and 1-methylazulene was prepared and run at 150°

	% Calculated by weight	% Calculated by mole	% Calculated by areas of graph
Azulene	78	80	77
1-Methylazulene	22	20	23

Control Experiment 2

A standard mixture of azulene, 1-methylazulene, and guaiazulene was prepared and run at 200°

	% (w/w)	% (mole/mole)	% calculated by areas of graph
Azulene	16	22	15
1-Methylazulene	22	26	23
Guaiazulene	61	52	61

Control Experiment 3

A standard mixture of azulene, 1-methylazulene, 4,6,8--trimethylazulene, and guaiazulene was prepared and analysed (at 200°) before, and after refluxing for 2½ hours in acetic acid, with subsequent working up in the manner described for the hydrocarbons analysed in section (CX).

	% by areas of graph before treatment	% by areas of graph after treatment
Azulene	16	15
1-Methylazulene	22	22
4,6,8-Trimethylazulene	31	30
Guaiazulene	32	33

The areas of the chromatograms were calculated by the recommended method[233] of multiplying the height of a peak by its breadth at a point 45.4% of the height from the base line.

The above figures show that the response appears to be with respect to the weight of each component rather than its mole proportion, but the experimental accuracy does not permit of a definite decision. Experienced users of this technique quote the standard error in quantitative analyses

as about 3-4% in the proportion of each component[234].

LITERATURE CITED

Abbreviations Used

Acta Chim Scand	Acta Chemica Scandinavica
Angew. Chem.	Angewante Chemie
Ann.	Liebig's Annalen der Chemie
Arch. Pharm.	Archiv der Pharmazie
Arzneimittel-Forsch.	Arzneimittel-Forschung
Ber.	Berichte der deutschen Chemischen Gesellschaft. (Discontinued with Vol. 77, 1944; continued as Chemische Berichte with Vol. 80, 1947)
Bull. Soc.	Bulletin de la Societe chimique de France
Bull. Inst. Phys. Chem.	Bulletin of the Institute of Physical and Chemical Research, Tokyo
C.A.	American Chemical Abstracts
Chem. Ind.	Chemistry & Industry
Chem. News	Chemical News
Chem. Rev.	Chemical Reviews. (Published by the American Chemical Society)
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemical Communications
Compt. rend.	Comptes rendus hebdomadaires des Seances de l'Academie des Sciences
Croatica Chem. Acta	Croatica Chemica Acta
Dewar	Dewar, "The Electronic Theory of Organic chemistry", 1st Edition, Oxford University Press.
Doklady Akad. Nauk.	Doklady Akademii Nauk S.S.S.R.
E.T.H., Zürich	Eidgenossischen Technischen Hochschule, Zürich

Experimentia	Experimentia
Ginsburg	"Non Benzenoid Aromatic Compounds", Edited by David Ginsburg, Interscience Publishers Ltd., 1959.
G.P.	German Patent
Helv. Chim. Acta	Helvetica Chimica Acta
Inorg. Syn.	Inorganic Syntheses
Izvest. Akad. Nauk.	Izvestiya Akademii Nauk S.S.S.R., Otdelenie Khimicheskikh Nauk. Moscow
J.	Journal of the Chemical Society
J.A.C.S.	Journal of the American Chemical Society
J. Chem. Phys.	Journal of Chemical Physics
J. Org. Chem.	Journal of Organic Chemistry
Nature	Nature
Naturwiss.	Naturwissenschaften
Org. Syn.	Organic Syntheses, Chapman & Hall Ltd.
Pauling	Pauling, "The Nature of the Chemical Bond", Cornell, 1938
Pharmazie	Pharmazie
Pharm. Bull.	Pharmaceutical Bulletin, Japan
Proc. Chem. Soc.	Proceedings of the Chemical Society
Proc. Jap. Akad.	Proceedings of the Japan Academy
Q. Rev.	Quarterly Reviews (Published by the Chemical Society)
Rev. Sci. Instr.	Review of Scientific Instruments
Sci. Papers Inst. Phys. Chem.	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo

Schweiz. Med. Woch.	Schweizerische Medizinische Wochenschrift
Tetrahedron	Tetrahedron. International Journal of Organic Chemistry
Tetrahedron Letters	Tetrahedron Letters
Trans. Farad. Soc.	Transactions of the Faraday Society
Vogel	Vogel, "A Text Book of Practical Organic Chemistry", Longmans, 1948
Weissberger	Weissberger, "Technique of Organic Chemistry, Vol. VII". 2nd Edition, Interscience Publishers Ltd., 1955
Z. Electrochem.	Zeitschrift für Electrochemie
Z. ges. Med.	Zeitschrift für die gesamte innere Medizin und ihre Grenzgebiete
Zhur. obshchei Khim.	Zhurnal obshchei Khimii
Z. Physik.	Zeitschrift für Physik
Z. Naturforsch.	Zeitschrift für Naturforschung

References

1. Piesse, Chem. News, 1863 8 245. Compt. rend., 1864, 57, 1016.
2. St. Pfau and Plattner, Helv. Chim. Acta., 1936, 19, 858.
3. Sherndal, J.A.C.S., 1915, 37, 167, 1537.
4. Ruzicka and Rudolph, Helv. Chim. Acta., 1926, 9, 118.
5. Plattner and St. Pfau, Helv. Chim. Acta., 1937, 20, 224.
6. Hückel, Gerke, and Gross, Ber. 1933, 66, 563.
7. Hückel and Schnitzspahn Ann. 1933, 505, 274.
8. Plattner, Helv. Chim. Acta., 1941, 24, 283E.
9. Plattner, Heilbronner, and Weber, Helv. Chim. Acta., 1949, 32, 574.
10. Stahl, Ber. 1954, 87, 202, 505.
11. Sorm, Benesova, and Herout, Coll. Czech. Chem. Comm. 1954, 19, 357.
12. Herout and Sorm, ibid., 1953, 18, 854.
13. Herout and Sorm, ibid., 1954, 19, 792.
14. Birch, Collins, and Penfold, Chem. Ind., 1955, 1773; Collins, J., 1959, 531.
15. Sorensen and Hougen, Acta Chim. Scand., 1948, 2, 447.
16. Prelog and Vaterlaus, Helv. Chim. Acta., 1950, 33, 2262.
17. Ikeda, Sci. Papers Inst. Phys. Chem., Tokyo, 1947, 42, 80. (C.A. 1949, 43, 81021.).
18. Mitui, Bull. Inst. Phys. Chem., Tokyo, 1941, 20, 549. (C.A. 1943, 37, 4071).
19. Bogs. and Meinhard, Pharmazie 1955, 10, 653; Plazo, Schweiz. med. Woch., 1951, 81, 110.

20. Kraul and Schmidt, Z. ges. Med. 1955, 10, 934; Anell, Arzneimittel-Forsch., 1955, 5, 721; Kraul and Schmidt, Arch. Pharm., 1957, 290, 66.

21. Hertz and Cleare, J.A.C.S., 1955, 77, 2318.

22. Plattner, Fürst, and Marti, Helv. Chim. Acta., 1949, 32, 2452.

23. Sorm and Fajkos, Coll. Czech. Chem. Comm., 1947, 12, 81.

24. Plattner, Heilbronner and Fürst, Helv. Chim. Acta., 1947, 30, 1100.

25. Plattern, Heilbronner, and Weber, Helv. Chim. Acta., 1952, 35, 1036.

26. Simon, Naville, Sulser, and Heilbronner, Helv. Chim. Acta., 1956, 39, 1107.

27. Anderson, Cowles, Tazuma, and Nelson, J.A.C.S., 1955, 77, 6321.

28. Knessl and Vlastiborova, Coll. Czech. Chem. Comm., 1954, 19, 782.

29. Herout, Romanuk, and Sorm, ibid., 1956, 21, 1359.

30. Romanuk, Herout, and Sorm, ibid., 1956, 21, 894.

31. Kallen and Heilbronner, Ginsburg, p. 323.

32. Morizur and Palland, Compt., rend., 1960, 251, 2043.

33. Plattner, Angew. Chem., 1942, 55, 131, 154.

34. Keller-Schierlein and Heilbronner, Ginsburg, p. 280-281, and references therein.

35. Ruzicka and Haagen-Schmidt, Helv. Chim. Acta., 1931, 14, 1104.

36. Sorm, Gut, Hlavnicka, Kucera, and Sedivy, Coll. Czech. Chem. Comm., 1951, 16, 168.

37. Meier, Thesis No. 2098, E.T.H., Zurich, 1954.

38. Plattner, Fürst, Gordon, and Zimmermann, Helv. Chim. Acta., 1950, 33, 1910.

39. Heilbronner, Plattner, and Wieland, Experimentia, 1947, 3, 70.

40. Lang and Froitzheim, G.P. 12583 IV b/12 o, 25 (1956).

41. Polyak and Prelog, Ginsberg, p. 281 and references therein.

42. Plattner and Wyss, Helv. Chim. Acta., 1941, 24, 483.

43. Plattner, Fürst, Müller and Keller, Helv. Chim. Acta., 1954, 37, 271.

44. Arnold, Ber., 1943, 76, 777.

45. Doering, Mayer, and DePuy, J.A.C.S., 1953, 75, 2386.

46. Reid, Stafford, and Ward, J., 1955, 1193.

47. Anderson and Tazuma, J.A.C.S., 1953, 75, 4979.

48. Doering and Wiley, Tetrahedron, 1960, 6, 190.

49. Rösler and König, Naturwiss., 1955, 42, 211.

50. Ziegler and Hafner, Angew. Chem., 1955, 67, 301.

51. Hafner, Angew. Chem., 1955, 67, 301.

52. Hafner, Ann., 1957, 606, 78.

53. Brunken and Poppe, Ber., 1960, 93, 2572.

54. Tilney-Bassett and Waters J., 1959, 3123.

55. Hafner, Angew. Chem., 1957, 69, 393.

56. Hafner and Kaiser, Ann., 1958, 618, 140.

57. Nozoe, Matsumara, Murase, and Seto, Chem. Ind. 1955, 1257; idem., Proc. Jap. Acad. 1956, 32, 339. For a review on this subject, see Nozoe, Croatica Chem. Acta., 1957, 29, 207.

58. Assony and Kharasch, Chem. Ind., 1954, 1388.

59. Assony and Kharasch, J.A.C.S., 1958, 80, 5978.

60. Reppe, Schlichting, and Meister, Ann., 1948, 560, 93.

61. Zeigenbein, Angew. Chem., 1958, 70, 106.

62. Pauson, Proc. Chem. Soc., 1960, 302.

63. Heilbronner, Ginsburg, Ch. V, and various references therein.

64. Plattner and Heilbronner, Helv. Chim. Acta., 1948, 31 804.

65. Heilbronner, Ginsburg, p. 229.

66. Heilbronner, Ginsburg, p. 234.

67. Müller, Thesis No. 2010, E.T.H., Zurich, 1951.

68. Plattner, Fürst, Müller, and Somerville, Helv. Chim. Acta., 1951, 34, 971.

69. Plattner, Heilbronner, Schmidt, Sandrin, and Fürst, Chem. Ind., 1954, 1202.

70. Heilbronner and Schmidt, Helv. Chim. Acta., 1954, 37, 2018.

71. Hafner and Bernhard, Ann., 1959, 625, 108.

72. Treibs, Neupert, and Hiebsch, Ber., 1959, 92, 141.

73. Treibs, Ann., 1957, 603, 145.

74. Arnold and Pahls, Ber., 1956, 89, 121.

75. Hafner and Veldes, Ann., 1957, 606, 90.

76. Treibs, Quarg, and Poppe, Ann., 1956, 598, 32.

77. Bergmann and Ikan J.A.C.S., 1956, 78, 1482.

78. Braude, Experimentia 1955, 11, 457.

79. Heilbronner and Wieland, Helv. Chim. Acta., 1947, 30, 947.

80. Kremers, J.A.C.S., 1923, 45, 717.

81. Pommer, Angew. Chem., 1950, 62, 281.

82. Kekule, Bull. Soc., 1865, 3, 98; Ann., 1866, 137, 169.

83. Erlenmeyer, Ann. 1866, 137, 327.

84. Dewar, p. 162.

85. Elvidge and Jackmnan, J., 1961, 859.

86. Armit and Robinson, J., 1925, 127, 1604.

87. Hückel, Z. Physik, 1931, 70, 204; 72, 310; 1932, 76, 626; Z. Electrochem., 1937, 43, 752, 857.

88. Pauling, and numerous references therein. See also reference 172.

89. Coulson, Q. Rev., 1947, 1, 144; Brown, Q. Rev., 1952, 6, 63, and numerous references in both of these.

90. Breslow and Yuan, J.A.C.S., 1958, 80, 5991.

91. Breslow and Höver, J.A.C.S., 1960, 82, 2644.

92. Farnum and Burr, J.A.C.S., 1960, 82, 2651.

93. Breslow and Battiste, Chem. Ind., 1958, 1143.

94. Breslow and Gal, J.A.C.S., 1959, 81, 4747.

95. Breslow, Haynie, and Mirra, J.A.C.S., 1959, 81, 247.

96. Volp'in, Koreshkov, and Kursanov., Izvest. Akad. Nauk., 1959, 560. (C.A. 1959, 53, 21799f).

97. Winstein, Shatavsky, Norton, and Woodward, J.A.C.S., 1955, 77, 4183.

98. Thiele, Ber., 1901, 34, 68.

99. Goss and Ingold, J., 1928, 1268.

100. Thiele and Balhorne, Ann., 1906, 348, 1.

101. Thiec and Wiemon, Bull. Soc., 1956, 177.

102. Doering and DePuy, J.A.C.S., 1953, 75, 5955.

103. Spooncer, Ph.D. Thesis, University of Washington, 1955.

104. Ramirez and Levy, J. Org. Chem., 1956, 21, 488.

105. Ramirez and Levy, J.A.C.S., 1957, 79, 67.

106. Armit and Robinson, J., 1922, 121, 827.

107. Allen and Van Allan, J.A.C.S., 1950, 72, 5165.

108. Kealy and Pauson, Nature, 1951, 168, 1039.

109. Woodward, Rosenblum, and Whiting, J.A.C.S., 1952, 74, 3458.

110. Nesmeyanov, Perevalova, Golovnya, Nikitina, and Simukova, Izvest. Akad. Nauk., 1956, 739. (C.A. 1957, 51, 1945b).

111. Fischer and Seus, Z. Naturforsch 1954, 9b, 386.

112. Osgerby and Pauson, J., 1958, 656.

113. Merling, Ber., 1891, 24, 3108.

114. Doering and Knox, J.A.C.S., 1954, 76, 3203.

115. Doering and Detert, J.A.C.S., 1951, 73, 876.

116. Giacomo and Smyth, J.A.C.S., 1952, 74, 4411.

117. Avram, Marica, and Nenitzescu, Ber., 1959, 92, 1088.

118. Katz, J.A.C.S., 1960, 82, 3784.

119. Craig, Chem. Rev., 1951, 49, 103.

120. Sondheimer and Gaoni, J.A.C.S., 1960, 82, 5765.

121. Reid, "Azulene and Related Substances", Chem. Soc. Special Publication No. 12, 1958, p. 69.

122. Sondheimer and Wolovsky, Tetrahedron Letters, 1959, No. 3, 3.

123. Sondheimer and Wolovsky, J.A.C.S., 1959, 81, 4755.

124. Mislow, J. Chem. Phys., 1952, 20, 1489.

125. Sondheimer, Wolovsky, and Gaoni, J.A.C.S., 1960, 82, 755.

126. Reid and Stafford, Chem. Ind., 1954, 277.

127. Galloway, Reid, and Stafford, Chem. Ind., 1954, 724.

128. Wheland and Mann, J., Chem. Phys., 1949, 17, 264.

129. Aitken and Reid, J., 1956, 3487.

130. Dewar, J.A.C.S, 1952, 74, 3345.

131. Coulson and Longuet-Higgins, Rev. Sci. Instr., 1947, 85, 927.

132. Brown, Trans. Farad. Soc., 1948, 44, 984.

133. Peters, J., 1958, 1028.

134. Julg, Thesis, University of Paris, 1955; Compt. rend. 1954, 239, 1498.

135. Dewar and Pettit, J., 1954, 1617.

136. Peters, J., 1958, 1023.

137. Kovats, Gunthard, and Plattner, Helv. Chim. Acta., 1955, 38, 1912.

138. Simonetta and Schomaker J., Chem. Phys., 1951, 19, 649.

139. Anderson, Nelson, and Tazuma, J.A.C.S., 1953, 75, 4980.

140. Heilbronner and Simonetta, Helv. Chim. Acta., 1952, 35, 1049.

141. Danyluk and Schneider, J.A.C.S., 1960, 82, 997.

142. Treibs and Ziegenbein, Ann., 1954, 586, 194.

143. Scheibli, Thesis No. 2134, E.T.H., Zurich, 1952.

144. Gerson, Schultz, and Heilbronner, Helv. Chim. Acta., 1958, 41, 1463.

145. Gerson, Gaümann, and Heilbronner, Helv. Chim. Acta., 1958, 41, 1481.

146. Gerson and Heilbronner, Helv. Chim. Acta., 1958, 41, 2332.

147. Gerson, Schultz, and Heilbronner, Helv. Chim. Acta., 1960, 43, 517.

148. Reid, Stafford, and Stafford, J., 1958, 1118.

149. Anderson and Nelson, J.A.C.S., 1950, 72, 3824.

150. Treibs and Ortmann, Naturwiss., 1958, 45, 85.

151. Treibs, Ber., 1959, 92, 2152.

152. Treibs, Neupert, and Hiebsch, Ber., 1959, 92, 1216.

153. Hafner, Angew. Chem., 1958, 70, 413.

154. See Reference 148.

155. Treibs, Hiebsch, and Neupert, Ber., 1959, 92, 606.

156. Vilsmeir and Haack, Ber., 1927, 60, 119.

157. Treibs, Ber., 1957, 90, 761.

158. Anderson, Scotoni, Cowles, and Fritz, J. Org. Chem., 1957, 22, 1193.

159. Zimmermann, Thesis No. 2199, E.T.H., Zurich, 1953.

160. Treibs and Schroth, Ann., 1954, 586, 202.

161. Miyazaki, Watnabe, Hashi, and Ukita, Pharm. Bull. 1957, 5, 417. (C.A. 1958, 52, 9058f).

162. Anderson and McDonald, J.A.C.S., 1959, 81, 5669.

163. Anderson, Anderson, and Replog, Proc. Chem. Soc., 1960, 72.

164. Hafner, Angew. Chem., 1958, 70, 419.

165. Senf, Thesis, Marburg, 1958. See Reference 164.

166. Mühlstädt, Treibs, and Mohr, Ber., 1961, 94, 808.

167. Hafner and Moritz, Angew. Chem., 1960, 72, 918.

168. Anderson and Replog, J. Org. Chem., 1960, 25, 1275.

169. Berthier and Pullmann, Compt. rend., 1949, 229, 761.

170. Reid, Stafford and Ward, J., 1958, 1100.

171. Hafner, Angew. Chem., 1961, 73, 29.

172. Wheland, J.A.C.S., 1942, 64, 900; "Resonance in Organic Chemistry", John Wiley, New York, 1955.

173. Coulson, Trans. Farad. Soc., 1947, 42, 265.

174. Anderson and Chang, J. Org. Chem., 1958, 23, 151.

175. Reid, Stafford, Stafford, and (in Part) McLennan and Voigt, J., 1958, 1110.

176. Kirby and Reid, J., 1961, in press.

177. Cookson, Rosenbaum, and Symons, Proc. Chem. Soc., 1960, 353.

178. D. H. Reid, unpublished results.

179. Claisen and Stylos, Ber., 1888, 21, 1144.

180. Hunsberger, J.A.C.S., 1950, 72, 5626.

181. Shigorin, Doklady Akad. Nauk., 1954, 96, 769. (C.A. 48, 11191 b).

182. Hergert and Kurth, J.A.C.S., 1953, 75, 1622.

183. Kirby and Reid, J., 1960, 494.

184. Arnold and Pahls, Ber., 1954, 87, 257.

185. Blout, Fields, and Karplus, J.A.C.S., 1948, 70, 194.

186. Kirby and Reid, J., 1961, 163.

187. Poppe and Treibs, Naturwiss., 1958, 45, 517.

188. Stepanow and Aldanowa, Angew. Chem., 1959, 71, 125.

189. Stepanow and Aldenowa, Zhur obschei. Khim., 1959, 29, 339. (C.A. 1960, 462f).

190. Bach, Poppe, and Treibs, Naturwiss., 1958, 45, 517.

191. Kirby and Reid, J., 1961, 1724.

192. Kirby and Reid, Tetrahedron Letters, 1960, 27, 1-4.

193. Corwin and Andrews, J.A.C.S., 1937, 59, 1973.

194. Fischer and Heyse, Ann., 1924, 439, 246.

195. Kirby and Reid, Chem. Ind., 1960, 1217.

196. Hafner and Pelster, Angew. Chem., 1960, 72, 781.

197. See Tetrahedron 1959 No. 2 and 3, for report on recent conference on "Hyperconjugation and its Applications", held at Indiana University, 2-4, June, 1958.

198. Berliner and Chen, J.A.C.S., 1958, 80, 343.

199. Heilbronner, Ginsburg, p. 236.

200. McEwan, J.A.C.S., 1936, 58, 1124.

201. Hine and Hine, J.A.C.S., 1952, 74, 5266.

202. Seubold, J.A.C.S., 1955, 77, 156.

203. Roberts, Webb, and McKlhill, J.A.C.S., 1950, 72, 408.

204. Günthard and Plattner, Helv. Chim. Acta., 1949, 32, 284.

205. Cross, "Introduction to Practical Infra-Red Spectroscopy", Butterworths Scientific Publications, 1960.

206. Bonthrone and Reid, J., 1959, 2773; Chem. Ind., 1960, 1192.

207. Braude,, Jackmann, and Linstead, J., 1954, 3548, 3564.

208. Dauben, Gadecki, Harmon, and Pearson, J.A.C.S., 1957, 79, 4557.

209. Dauben and Honnen, J.A.C.S., 1958, 80, 5570.

210. Fuson, Ross, and McKeever, J.A.C.S., 1938, 60, 2935.

211. Linstead and Thomas, J., 1940, 1130.

212. Diels and Alder, Ber. 1927, 60, 716.

213. Schneider and Sack, Ber., 1923, 56, 1786.

214. Schneider and Seebach, Ber., 1921, 54, 2285.

215. Arndt, Eistert, Scholz, and Aron, Ber., 1936, 69, 2373.

216. Baeyer, Ber., 1910, 43, 2337.

217. Baeyer and Piccard, Ann., 1911, 384, 208.

218. Org. Syn. 23, 98.

219. Hofmann and Kirmreuther, Ber., 1909, 42, 4856.

220. Baeyer, Ber., 1905, 38, 586.

221. Vogel, p. 740.

222. Gomberg and Cone, Ann., 1909, 370, 195.

223. Burton and Cheeseman, J., 1955, 3089.

224. Andrews and Kaeding, J.A.C.S., 1951, 73, 1007.

225. Baeyer and Villiger, Ber., 1902, 35, 1189.

226. Lifschitz and Girbes, Ber., 1928, 61, 1485.

227. Burton and Cheeseman, J., 1953, 832.

228. Inorg. Syn. 1, p. 47.

229. Auwers and Schmidt, Ber., 1925, 58, 528.

230. Borsche, Ann., 1910, 377, 84.

231. Vogel, p. 167.

232. Weissberger, p. 334.

233. Jaulmes and Mestres, Compt. rend., 1959, 248, 2752.

234. James, "Methods of Biochemical Analysis", Ed. Glick, Interscience Publishers, 1960, VIII, 1.

235. Org. Syn. Collected Vol. 3, p. 392.

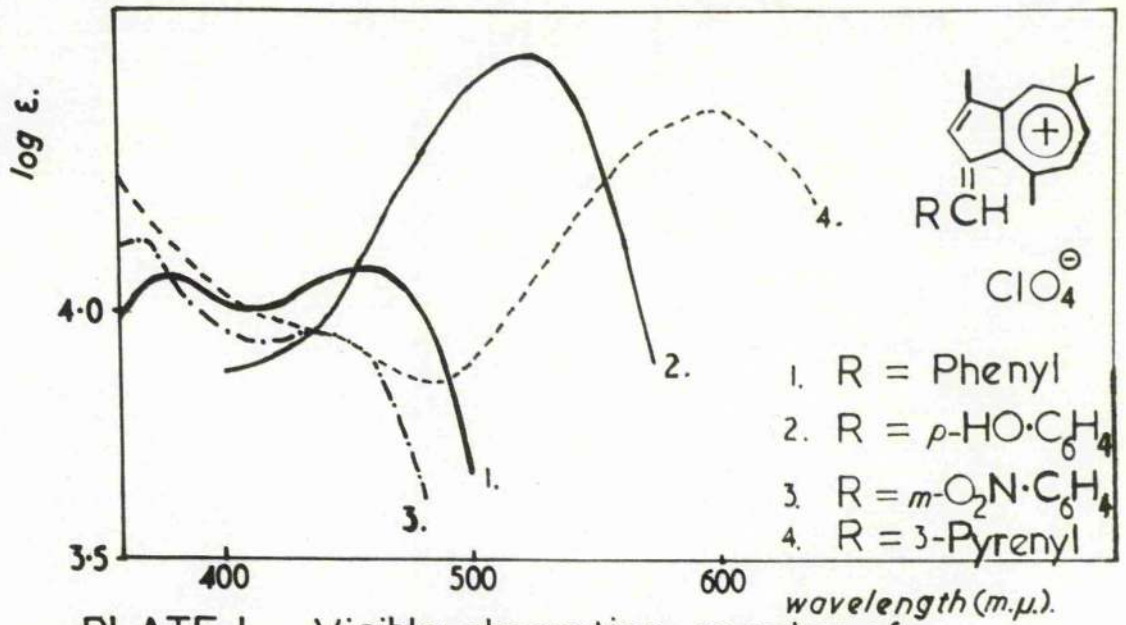


PLATE I. Visible absorption spectra of 3-(R-methylene)guaiazulenium perchlorates in CH_3COOH.

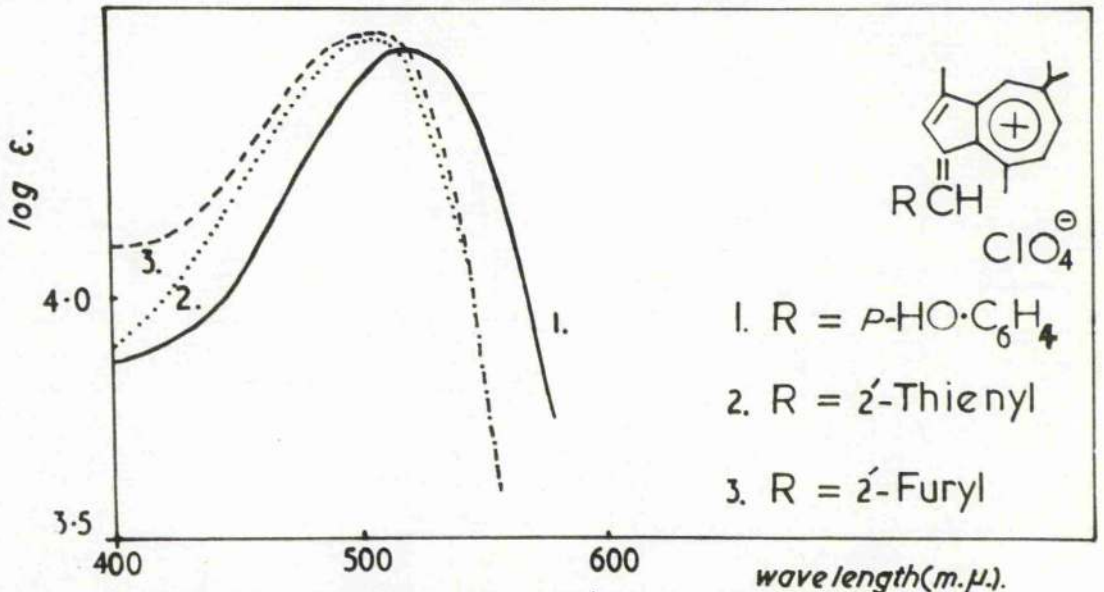


PLATE II. Visible absorption spectra of 3-(R-methylene)guaiazulenium perchlorates in CH_3COOH.

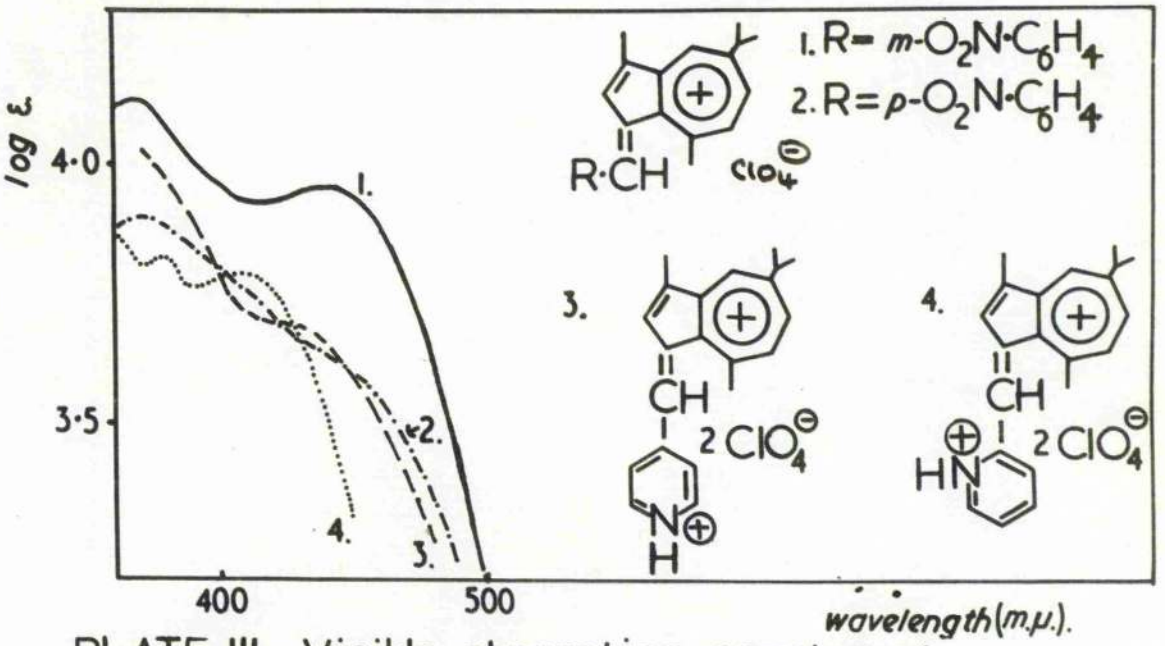


PLATE III. Visible absorption spectra of 3-(R-methylene)guaiazulenium perchlorates in CH_3COOH.

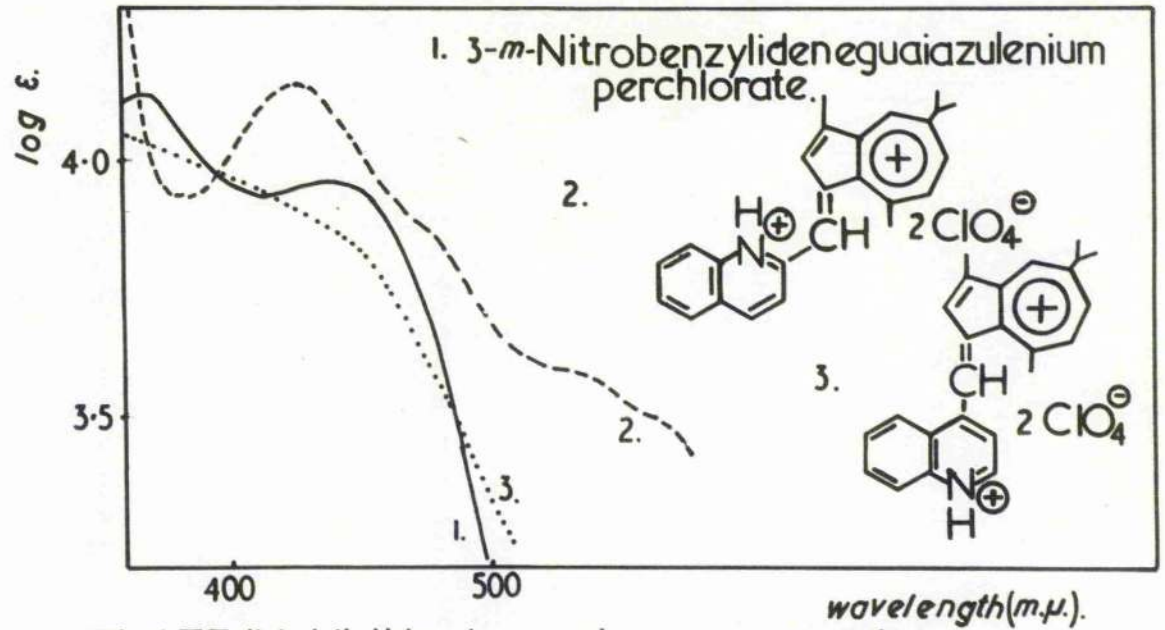


PLATE IV. Visible absorption spectra of 3-(R-methylene)guaiazulenium perchlorates in CH_3COOH.

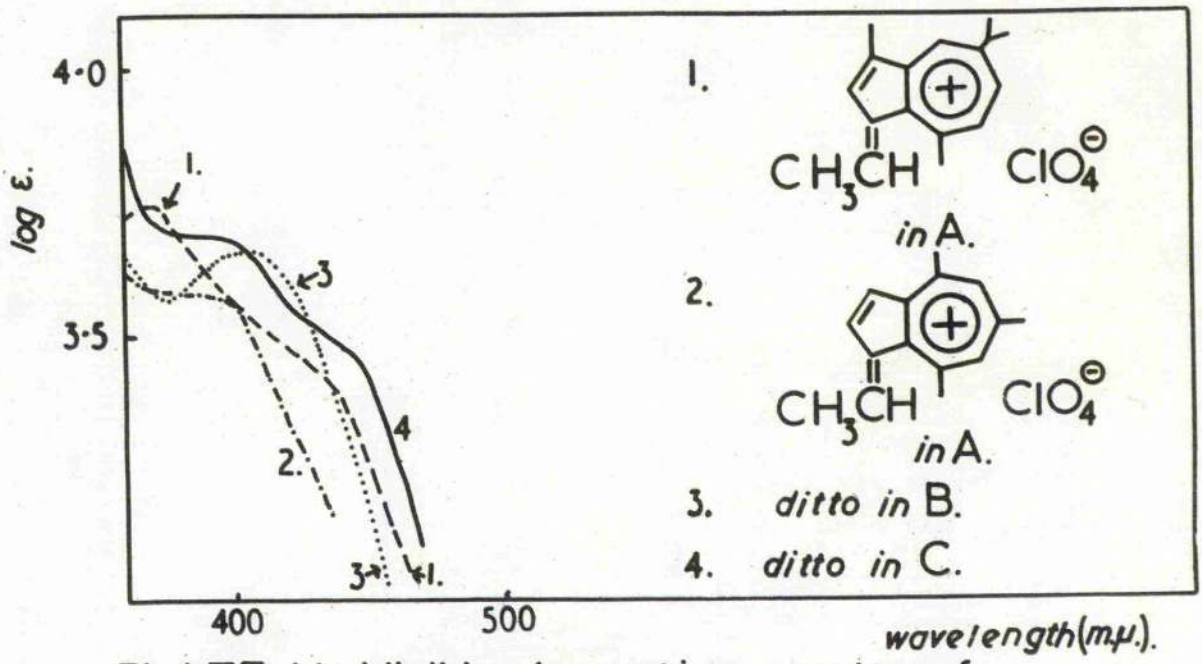


PLATE V. Visible absorption spectra of 1(3)-ethylideneazulenium perchlorates.

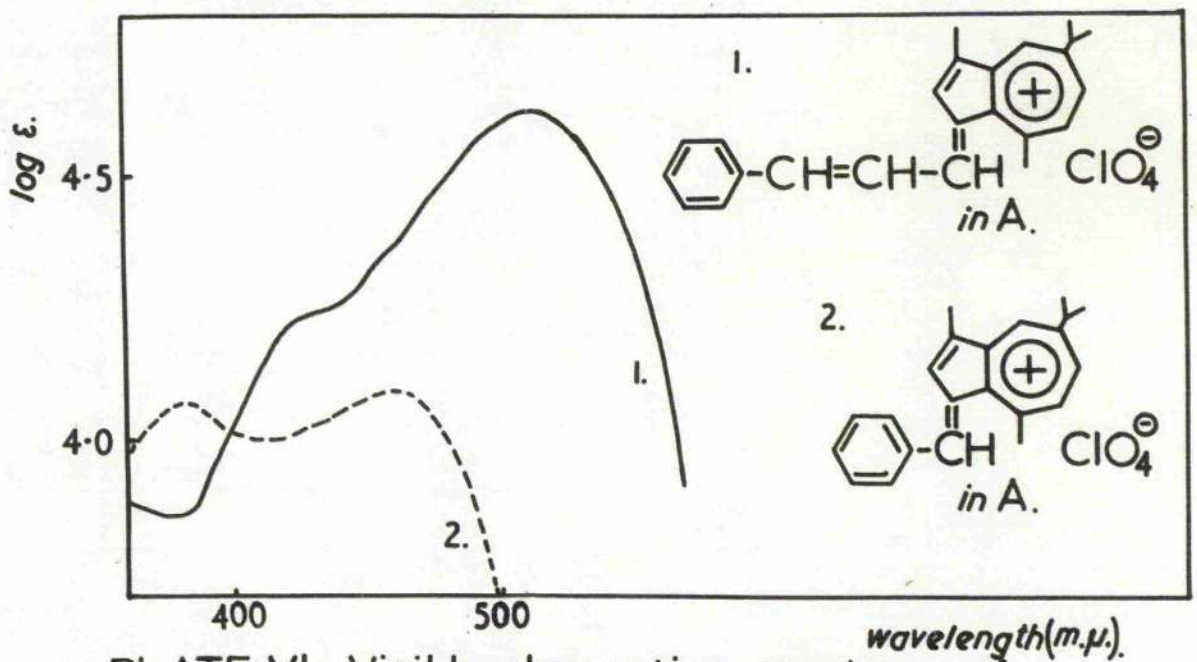


PLATE VI. Visible absorption spectrum of 3-cinnamylideneguaiazulenium perchlorate.

A- *Acetic acid.* B- *Acetonitrile.*

C- *Acetic acid containing* 2% (v/v) *perchloric acid.*

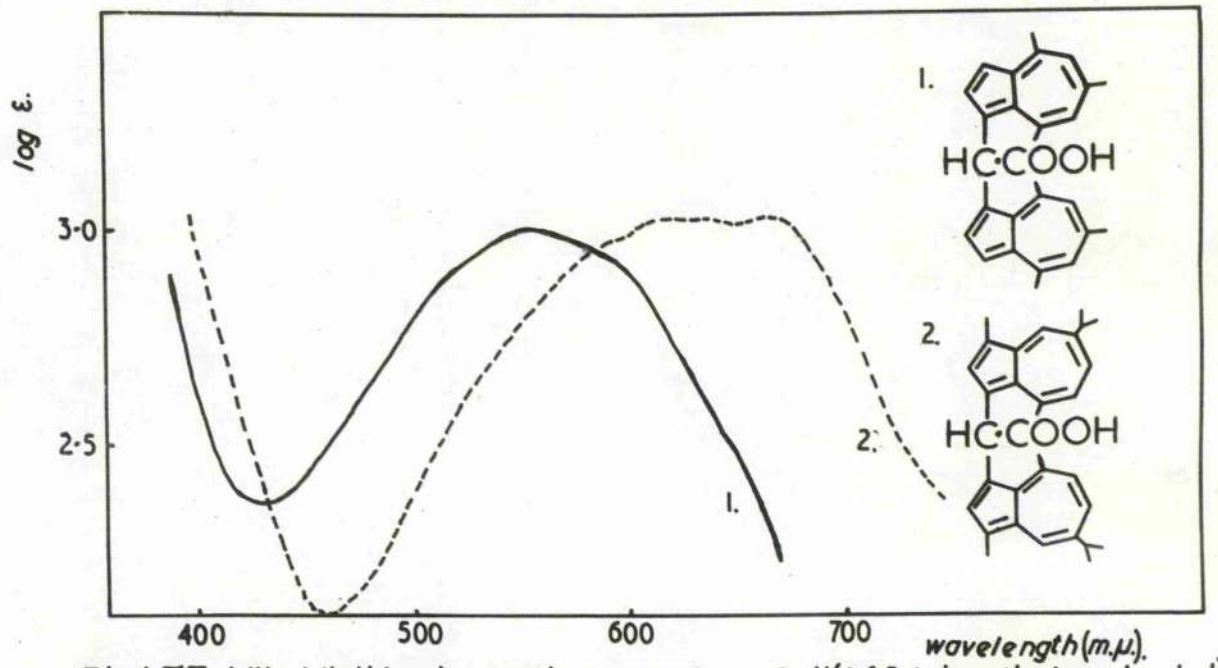


PLATE VII. Visible absorption spectra of di(4,6,8-trimethylazulen-1-yl)-acetic acid and 3,3'-diguaiazulenylacetic acid in acetonitrile.

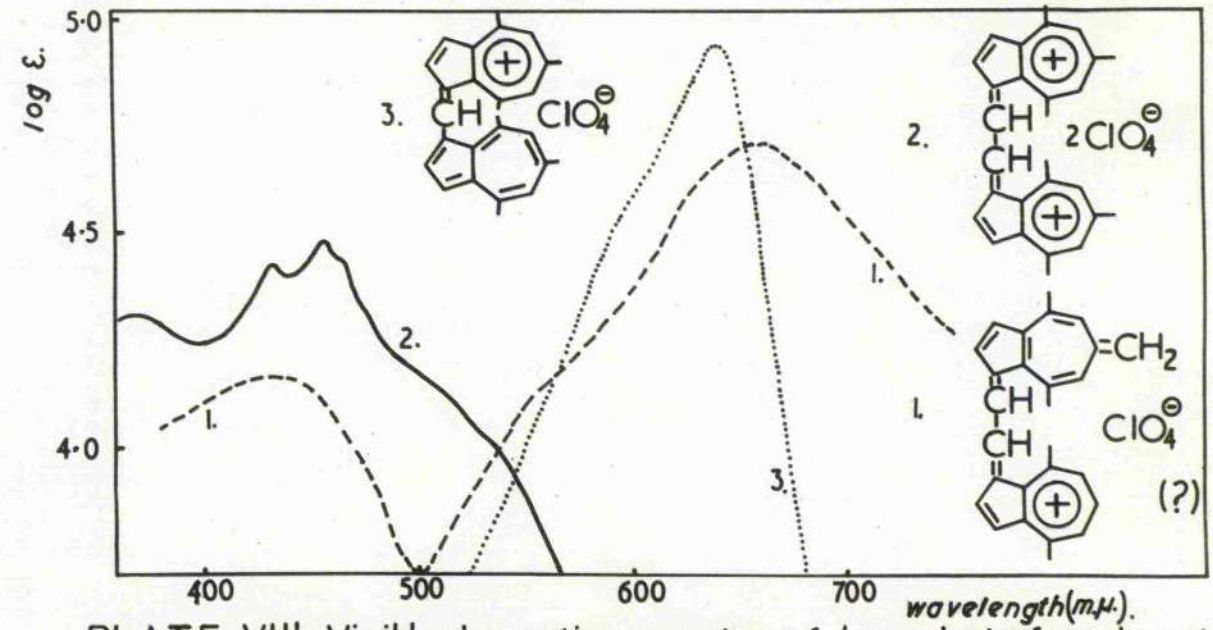


PLATE VIII. Visible absorption spectra of 1., product of condensation of 4,6,8-trimethylazulene with glyoxal and perchloric acid, in acetonitrile; 2., ditto, in acetonitrile containing 2% (v/v) perchloric acid; 3., 1-(4,6,8-trimethylazulen-1-yl)methylene-4,6,8-trimethylazulenium perchlorate, in acetic acid.

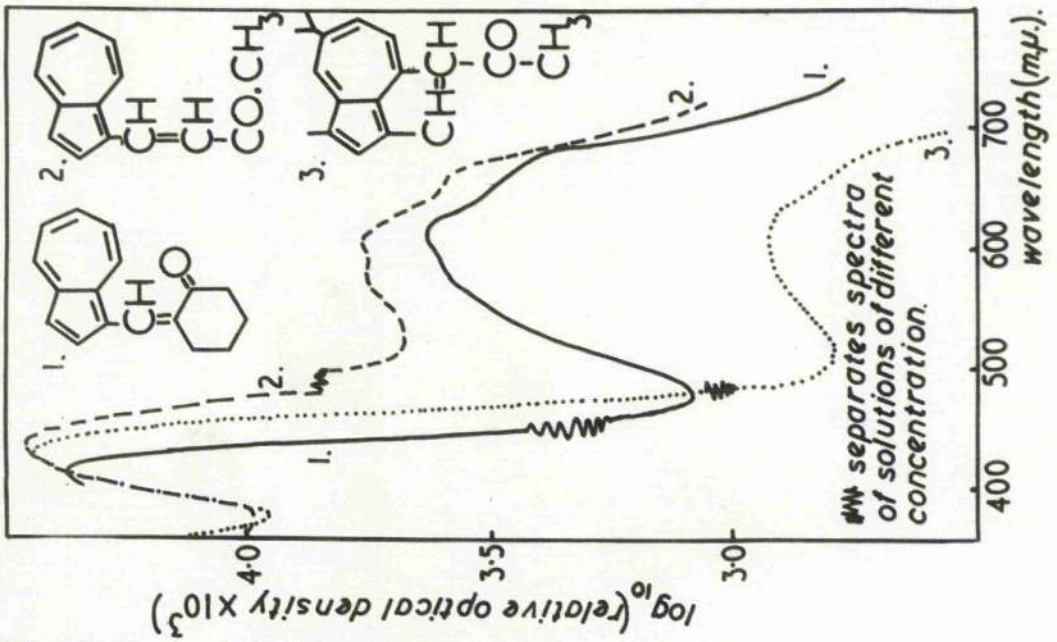


PLATE IX. Visible absorption spectra of 2-(azulen-1-yl)methyleneketones in benzene.

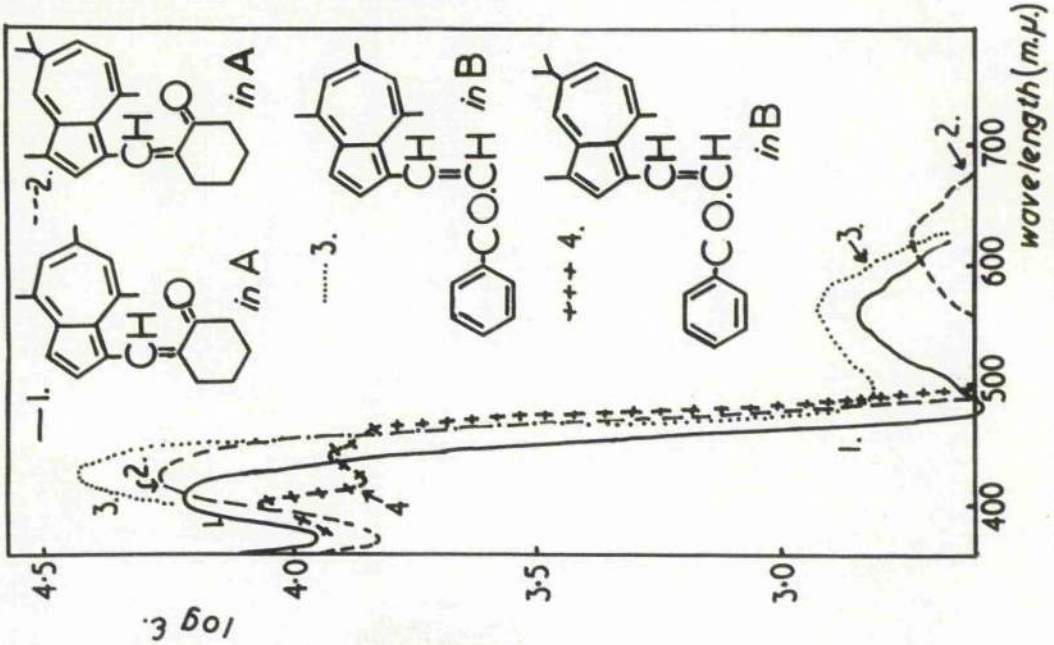


PLATE X. Visible absorption spectra of 2-(azulen-1-yl)methyleneketones.

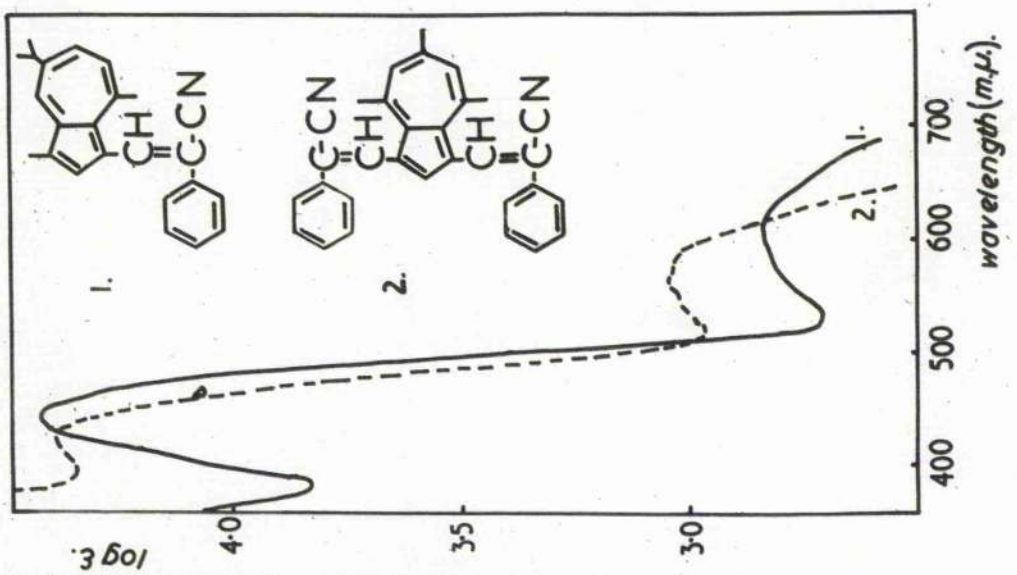


PLATE XI. Visible absorption spectra of 3-(2-cyano-2-phenylvinyl)-guaiazulene and 1,3-di(2-cyano-2-phenylvinyl)-4,6,8-trimethylazulene, in benzene.

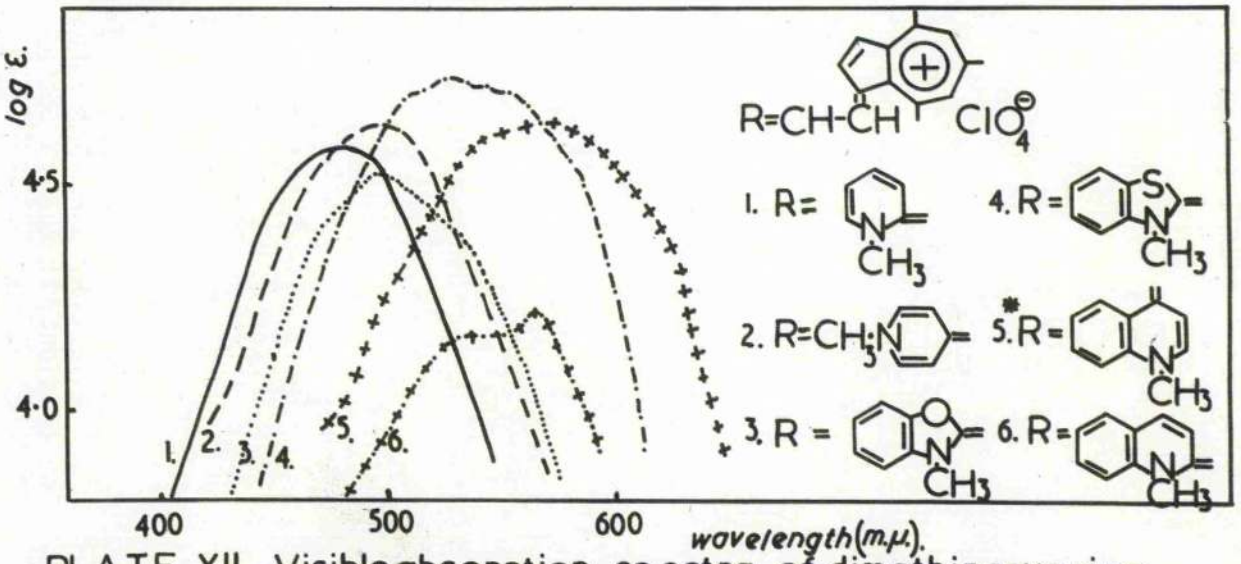


PLATE XII. Visible absorption spectra of dimethinecyanine salts from 1-formyl-4,6,8-trimethylazulene and heterocyclic quarternary ammonium salts, in methanol.

* *Iodide instead of perchlorate.*

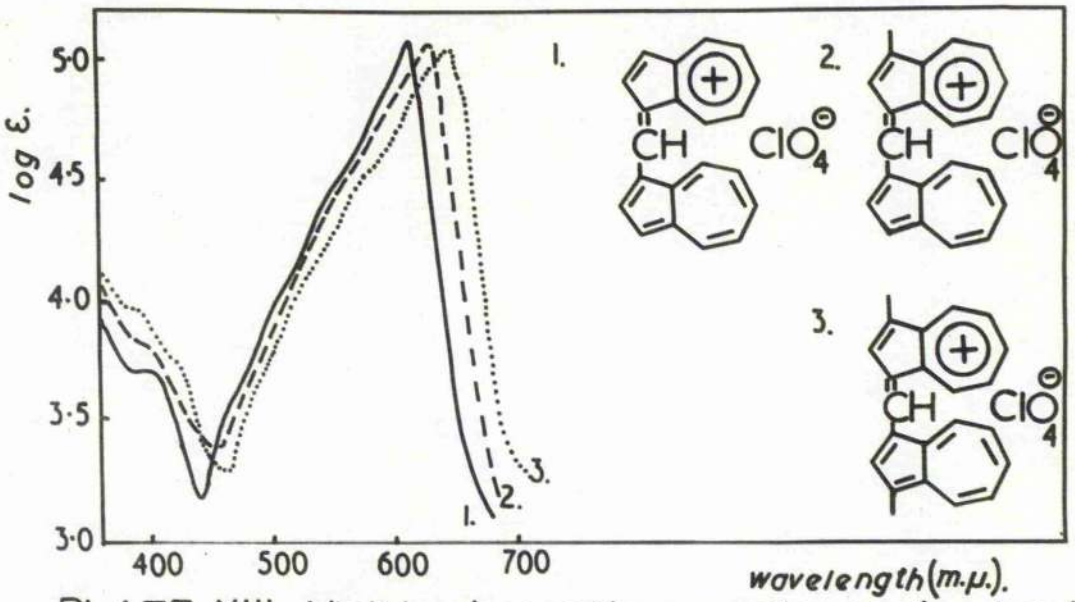


PLATE XIII. Visible absorption spectra of 1,1'-azulenylmethyleneazulenium perchlorates in acetic acid.*

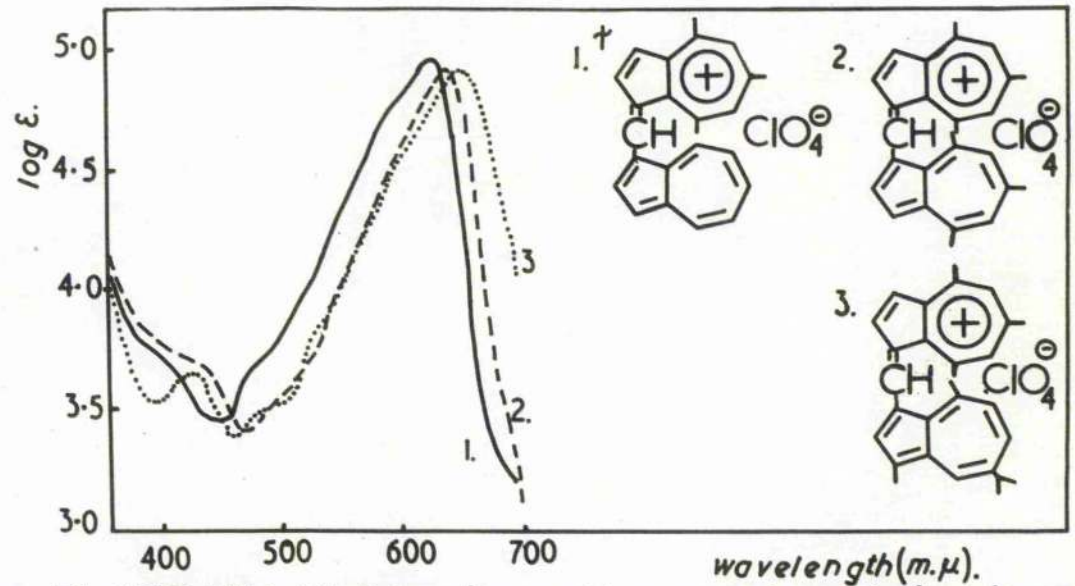


PLATE XIV. Visible absorption spectra of 1,1'-azulenylmethyleneazulenium perchlorates in acetic acid.

* *Containing 0·4% (v/v) acetonitrile.*

† *In acetic acid containing 4% (v/v) acetonitrile.*

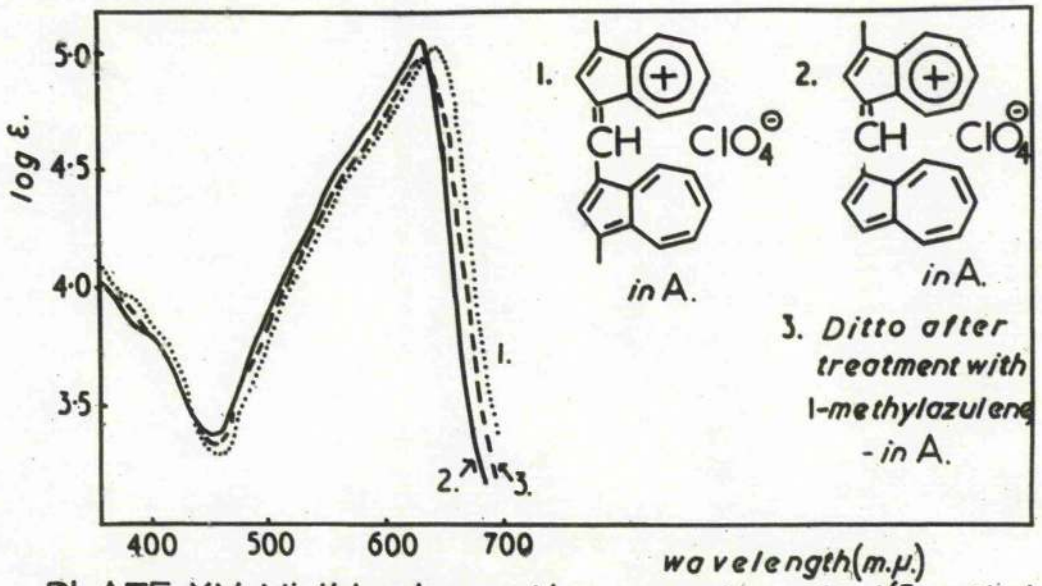


PLATE XV. Visible absorption spectra of 1., 1-(3-methylazulen-1-yl)methylene-3-methylazulenium perchlorate; 2., & 3., 1-(3-methylazulen-1-yl)methyleneazulenium perchlorate, before, & after boiling it with 1-methylazulene & acetic acid for 2 hrs. See (C.XI).

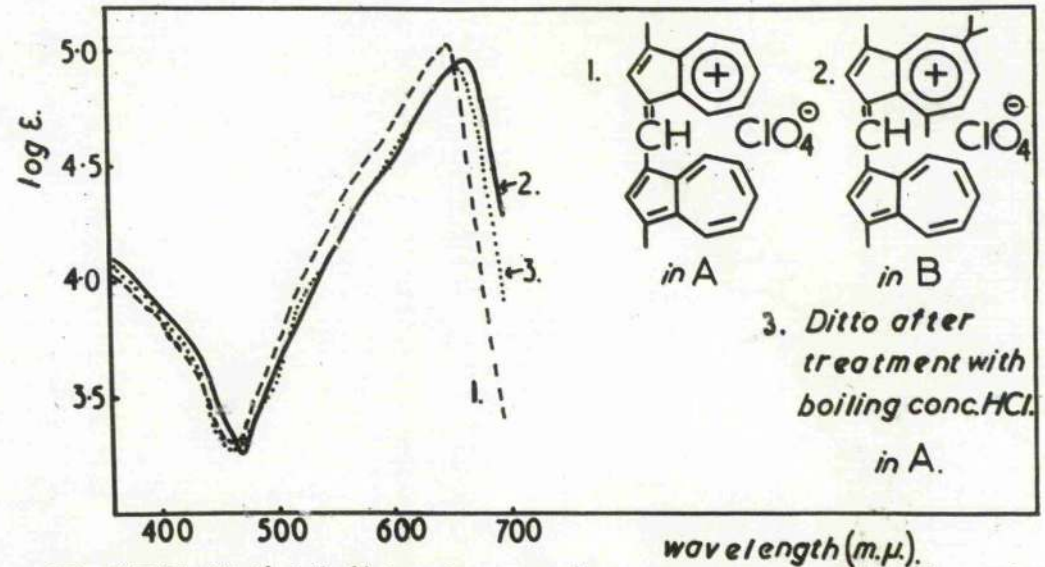


PLATE XVI. Visible absorption spectra of 1., 1-(3-methylazulen-1-yl)methylene-3-methylazulenium perchlorate; 2., & 3., 1-(guaiazulen-3-yl)methylene-3-methylazulenium perchlorate; before, & after being boiled with conc. HCl. for 2¼ hrs. See (C IX 7).

A *Acetic acid containing* 0·4% (v/v) *acetonitrile*. B *Acetic acid*.

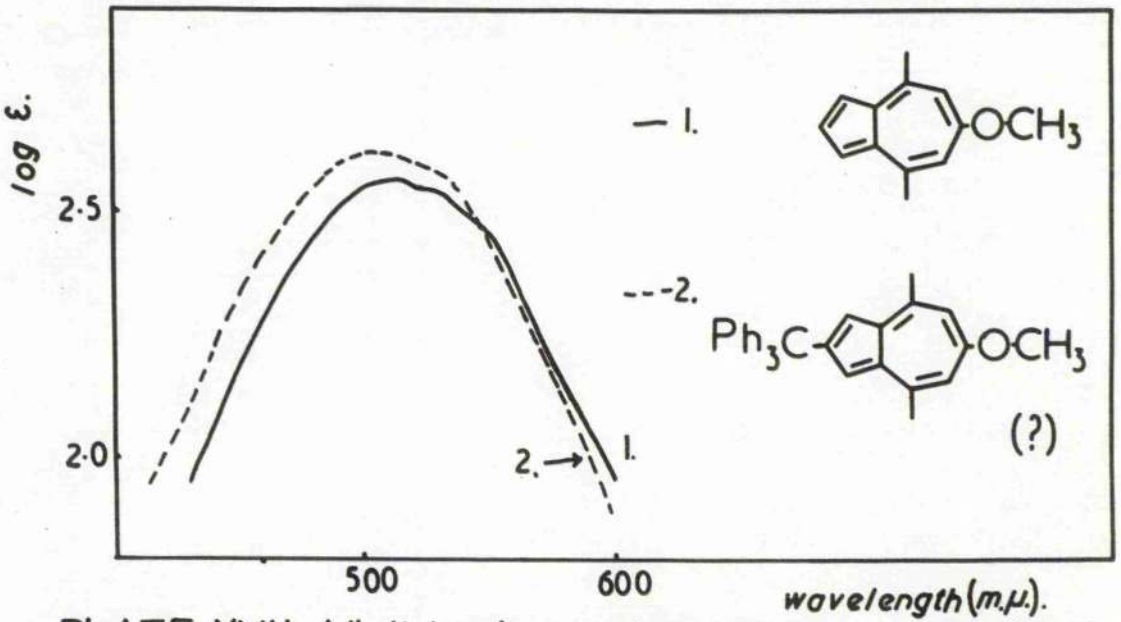


PLATE XVII. Visible absorption spectra of 4,8-dimethyl--6-methoxyazulene, and the product of its reaction with triphenylmethyl perchlorate, in benzene.

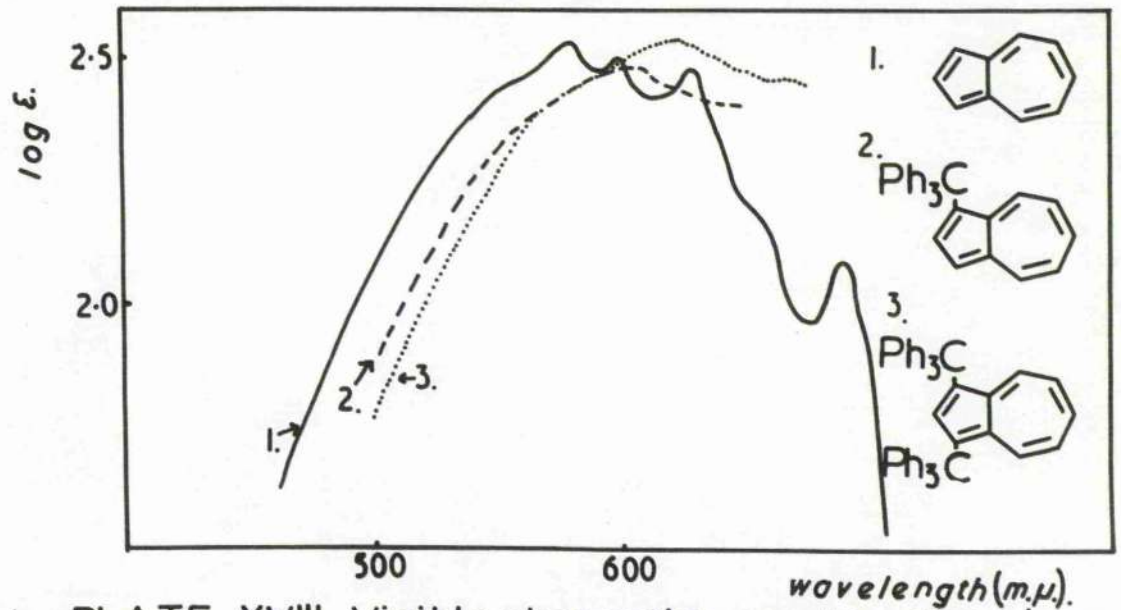


PLATE XVIII. Visible absorption spectra of azulene, 1-triphenylmethylazulene, and 1,3-bistriphenylmethyl-azulene, in benzene.

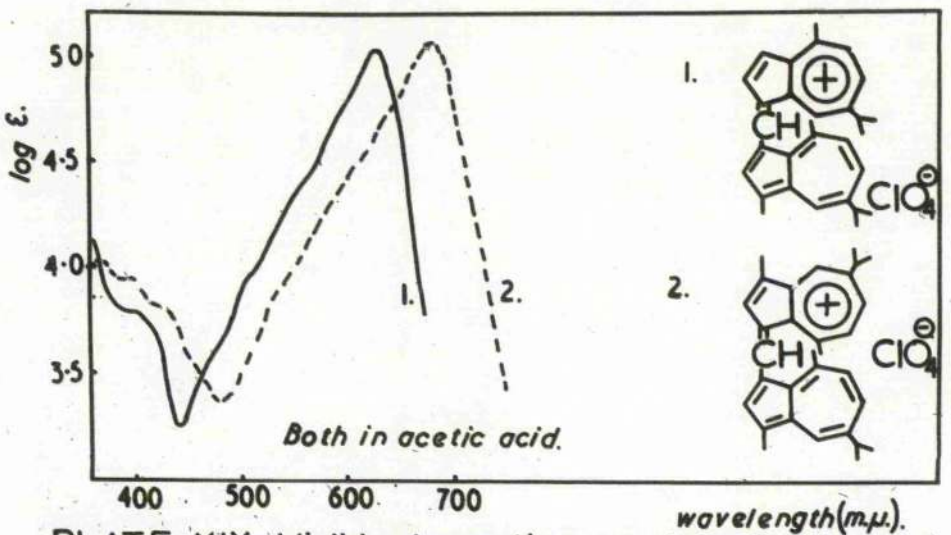


PLATE XIX. Visible absorption spectra of 1., the product of the reaction of guaiazulene with triphenylmethyl perchlorate (C,VIII,2), and 2., 3-(guaiazulen-3-yl)methyleneguaiazulenium perchlorate.

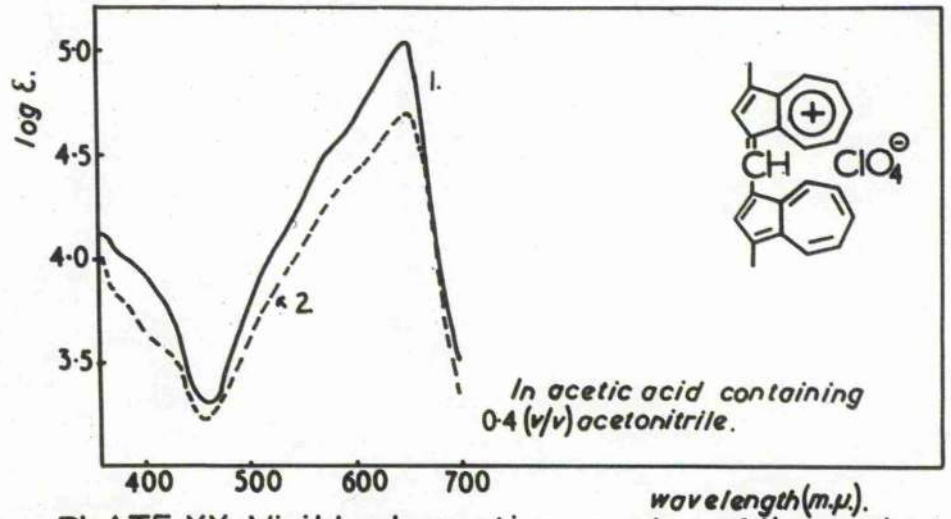


PLATE XX. Visible absorption spectra of the product of the reaction of 1-methylazulene with triphenylmethyl perchlorate; 1., with an excess of 1-methylazulene, and 2., with an excess of triphenylmethyl perchlorate. See (C,VIII,1).

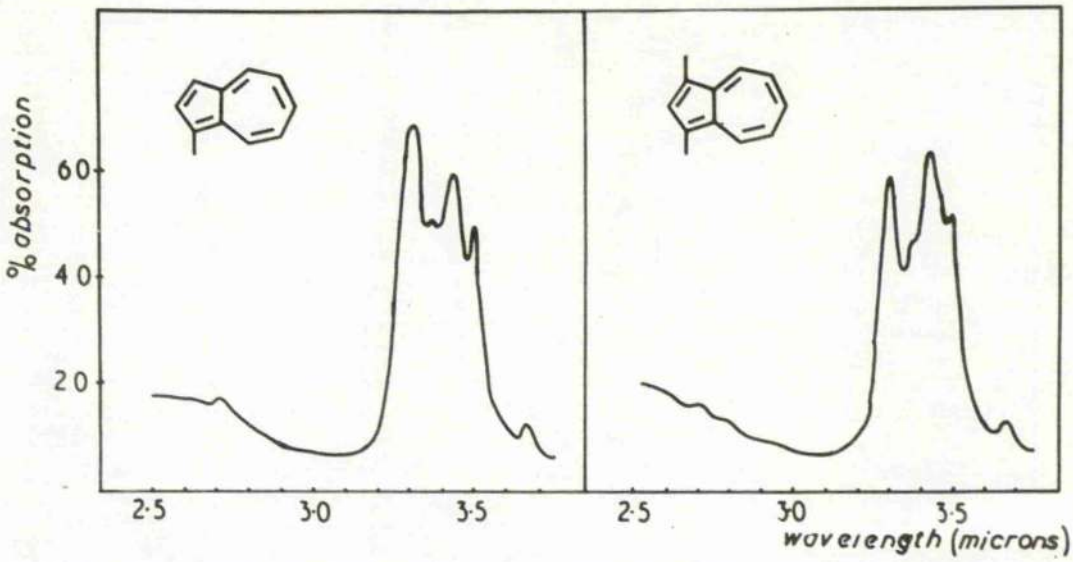


PLATE XXI. Infra-red absorption spectra of 1-methylazulene, and 1,3-dimethylazulene, in CCl_4.

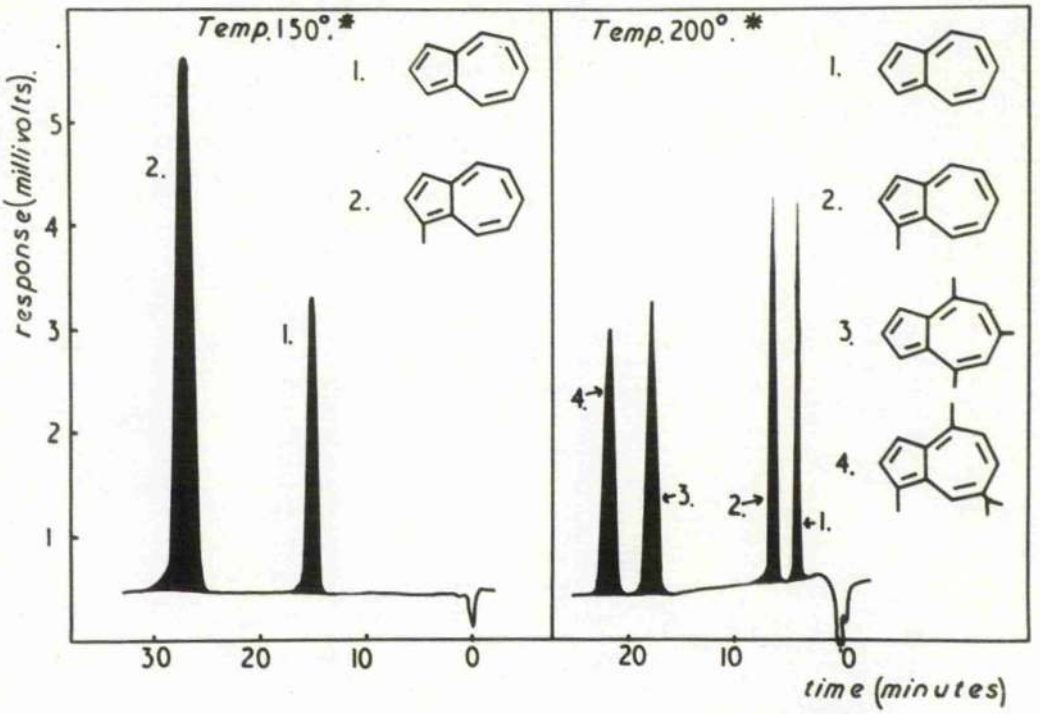


PLATE XXII. Typical gas-liquid chromatograms (of known mixtures) obtained during analysis of azulene mixtures.

* *For other data see appendix.*